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THE

PHYSICAL REVIEW.

AN EXTENSION OF THE ELECTRON THEORY OF METALS.

By A. E. Caswell.

Synopsis.

Theory of metallic conduction assuming free electrons and positive centers; comparison of computed with experimental results.—In the preceding theoretical paper the author has deduced a number of equations for the phenomena of thermoelectricity and metallic conduction. These are in fairly good agreement with the experimental facts within the range of ordinary temperatures, providing proper values are given to the constants for the various metals. To determine whether the values of the constants derived from one phenomenon will agree with those derived from other phenomena, the *constants for the thermo E.M.F., the Peltier E.M.F. and the Thomson E.M.F.* were computed from the experimental results for the thermoelectric power. While good agreement with observed values was found for the first two phenomena, for the Thomson E.M.F. and its temperature gradient the computed results frequently have the wrong sign, though they are of the right order of magnitude. The computed *variation of conductivity with temperature* agrees closely with the experimental results for copper for the range 0–70°, but the departures at higher temperatures are large and suggest that the equation needs modification. *Deduction. The concentration of free electrons and positive centers* computed from thermoelectric data, indicate that the observed differences of electrical conductivity among the various metals depend principally upon differences in the concentration of positive centers.

II. THERMOELECTRIC AND CONDUCTIVITY CONSTANTS.

Thermoelectric Constants.

ACCORDING to the theory advanced in the preceding paper, the number of free electrons in a unit volume of a substance, that is, the concentration, is given by the equation

$$N = ae^{xT}, \tag{9}$$

where T is the absolute temperature and x is a constant which may very appropriately be called the temperature coefficient of the concentration of the electrons. a also is a constant and obviously is the number of electrons at the absolute zero or the initial concentration.

Similarly, the concentration of the positive centers is given by the equation

$$n = be^{yT}, \tag{10}$$

where b is the initial concentration of the positive centers, also a constant, and y is the corresponding temperature coefficient of the concentration of positive centers, which is assumed to be constant.

The mean free path of the electrons depends upon the concentration of the positive centers and was expressed in terms of the constants c and y, the former being the mean free path at the absolute zero and dependent upon the value of b, thus:

$$\lambda = ce^{-yT}. \tag{11}$$

The ratio of the concentrations of the electrons in any two metals was given by the equation (following J. J. Thomson)

$$Q_{12} = \frac{2\alpha}{3\epsilon} \log (N_1/N_2), \tag{2}$$

where Q is the thermoelectric power between the metals denoted by the subscripts 1 and 2, α is the ratio of the kinetic energy of a molecule to the absolute temperature of the gas of which it forms a part, and ϵ is the charge on an electron.

The thermoelectric power is given by the equation

$$Q = A + BT, \tag{15a}$$

or the equivalent expression

$$Q = Q_0 + Bt. \tag{15b}$$

The constants A, B and Q_0 are connected by the relation

$$Q_0 = A + 273B, \tag{12c}$$

and t is the Centigrade temperature.

Since the Peltier E.M.F. satisfies the equation

$$P = QT, \tag{7}$$

both experimentally and theoretically, it follows that

$$P = AT + BT^2. \tag{12a}$$

The thermo E.M.F. is given by

$$E = Q_0 t + \tfrac{1}{2}Bt^2. \tag{16a}$$

The exponent x of equation (9) and σ, the coefficient of the Thomson effect, are connected by the relation

$$x = \frac{3\epsilon\sigma + \alpha}{2\alpha T}, \tag{24}$$

and the temperature gradient of the Thomson effect is given by the equation

$$\frac{d\sigma}{dT} = \frac{2\alpha x}{3\epsilon}. \tag{23}$$

Other relations which are used in computation are

$$a_1/a_2 = e^{2\epsilon A/2\alpha}, \tag{20}$$

$$x_1 - x_2 = 3\epsilon B/2\alpha, \tag{21}$$

and

$$\sigma_1 - \sigma_2 = BT. \tag{25a}$$

The data given in the first three columns of Table I. are taken from

TABLE I.

Thermoelectric Constants Computed from Thermoelectric Power.

Substance.	$Q_0 \times 10^6$.	$B \times 10^6$.	$A \times 10^6$.	a_1/a_2.	$x_1 - x_2 \times 10^4$.	$x \times 10^4$.	$\sigma \times 10^6$ at 0° C.	$\frac{d\sigma}{dT}$	$N_1 + N_2$ at 0° C.
Aluminium...	+ .76	−.0039	+ 1.82	1.021	− .45	17.86	− 1.065	.1539	1.009
Cadmium....	− 2.63	−.0424	+ 8.95	1.109	−4.91	13.40	−11.58	.1166	.969
Copper.....	− 1.34	−.0094	+ 1.22	1.014	−1.09	17.22	− 2.566	.1487	.986
Gold.....	− 2.80	−.0101	− .04	.999	−1.17	17.14	− 2.758	.1480	.968
Iron.....	−17.15	+.0482	−30.32	.738	+5.59	23.90	+13.17	.2047	.820
Lead.....	0	0	0	1.000	0	18.31	0	.1579	1.000
Magnesium ..	− 2.22	+.0094	− 4.78	.946	+1.09	19.40	+ 2.566	.1670	.975
Nickel.....	+21.8	+.0506	+ 8.00	1.097	+5.86	24.17	+13.80	.2070	1.287
Palladium....	+ 6.18	+.0355	− 3.51	.960	+4.12	22.43	+ 9.68	.1924	1.074
Platinum (hardened).	− 2.57	+.0074	− 4.59	.948	+ .86	19.17	+ 2.020	.1651	.971
Platinum (malleable).	+ .60	+.0109	− 2.37	.973	+1.26	19.57	+ 2.976	.1685	1.007
Silver.....	− 2.12	−.0147	+ 1.89	1.022	−1.70	16.61	− 4.01	.1435	.976
Steel.....	−11.17	+.0325	−19.97	.793	+3.77	22.08	+ 8.87	.1895	.879
Tin.....	+ .43	−.0055	+ 1.93	1.023	− .64	17.67	− 1.496	.1525	1.006
Zinc.....	− 2.32	−.0238	+ 4.18	1.050	−2.76	15.55	− 6.50	.1347	.974

Table 298, page 268 of the Smithsonian Physical Tables. Lead is taken as the standard substance and is denoted by the subscript 2, while the subscript 1 refers to the substance named in the first column. Q is positive when the current flows in the metal indicated by the subscript 1 from cold to hot, and σ is positive if the Thomson effect causes an evolution of heat when the current flows from hot to cold. The Thomson effect for lead is assumed to be zero at 0° C. Throughout the computations the value of the ratio $2\alpha/3\epsilon$ has been taken as 8.62×10^{-5} volts per Centigrade degree squared.

The numbers given in the fourth, fifth, sixth and eighth columns of the table were calculated from those in the second and third with the

aid of equations (12*c*), (20), (21) and (25*a*), respectively. The value of x, the temperature coefficient of concentration of the electrons, for lead was calculated by means of equation (24), and this together with the numbers in the sixth column give those in the seventh. The temperature gradients of the Thomson effect are given in the ninth column and, according to equation (23), are the products of the numbers in the seventh column and the ratio $2\alpha/3\epsilon$. They may also be obtained by adding $\alpha/3\epsilon$ to the numbers given in the eighth column and dividing the sum by 273. The numbers in the tenth column were calculated from those in the second with the aid of equation (2).

In Table I. Q_0, A and σ are expressed in volts per degree Centigrade, and B and $d\sigma/dT$ are expressed in volts per Centigrade degree squared. In Table II. the author has compiled the results obtained by a number of investigators, and for purposes of comparison has expressed these results in the same form as those calculated in Table I. In a few cases the temperature gradients could not be expressed as a simple number, so the number given is a fair approximation. A comparison of the values of σ, the coefficient of the Thomson effect, in the two tables shows that the computed values are of the same order of magnitude as the actual, with occasionally, perhaps accidentally, values which almost coincide. On the whole, however, corresponding values are about as apt to have the opposite as the same sign. The temperature gradients agree better as to sign, but the computed values are much larger than those observed. It may be noted that in most cases the calculated values of σ and those observed coincide within the range of ordinary temperatures. For example, taking three cases at random, we find that Cermak's value of the Thomson effect for aluminium coincides with the theoretical value at 5.1° C., Berg's for copper at 29.0° C., and Lecher's for copper at 25.2° C. In view of the fact that the Thomson effect is a small heating effect superimposed upon the larger Joule heating effect, it would not be surprising if the variation of the former with temperature would be very difficult to determine with any degree of accuracy. Furthermore, there are frequently very marked differences in the observed values of the Thomson effect for a metal, sometimes greater than that between different metals, due probably to differences in the methods employed in determining the effect and to differences in the specimens. Then, too, it must be borne in mind that the computed values are based on the thermo E.M.F.'s of entirely different specimens from those used in determining the Thomson effect. So we probably should not expect a much better agreement than that found.

In Table III. the values of the Thomson effect for a number of bismuth-

TABLE II.

Observed Values of the Thomson Effect.

Substance.	Reference.	$\sigma \times 10^8$ at 0° C.	$d\sigma/dT$.
Aluminium...	Cermak, Ann. d. Phys., 33, p. 1214, 1910.	− .272	−.00092
Cadmium....	Cermak.	+ 9.216	+.00642
Copper.....	Berg, Ann. d. Phys., 32, pp. 477–519, 1910.	+ 1.60	+.0048
"	King, Amer. Acad. Proc., 33, pp. 353–379, 1898.	+25.5	negative
"	Lecher, Ann. d. Phys., 20, pp. 480–502, 1906.	+ 1.260	+.00235
Iron.....	Berg, same as above.	− 4.00	−.833
"	Aalderink, Arch. Néedlandaises, 15, pp. 321–352, 1910.	+19.5	−.205
"	Battelli, Atti della R. Acc. dei Lincei, 3, p. 212, 1887.	−36.06	−.0463
"	Hall, Campbell, Serviss, Churchill, Amer. Acad. Proc., 42, pp. 579–626, 1907.	−88.92	+.2724
"	Konigberger and Weiss, Ann. d. Phys., 35, p. 1, 1911.	−11.32	....
"	Lecher, same as above.	−77.87	−.8614
Lead.....	Battelli, same as above.	+ .586	....
"	Cermak, same as above.	+ .092	+.00281
"	Le Roux.	0	....
Platinum.....	Berg, same as above.	− 9.10	varies
Silver.....	Hörig, Phys. Zeits., 14, p. 446, 1913.	+ 2.6	....
"	Lecher, same as above.	+ 3.085	+.00372
Tin.....	Cermak, same as above.	− .356	−.00105
Zinc.....	Cermak, same as above.	+ 2.60	+.00264

tin alloys as experimentally determined by the author[1] and the corresponding values as computed from the observed thermo E.M.F.'s are given. The thermo E.M.F.'s were in each case the mean of the values for two specimens of the same percentage, but these specimens sometimes

TABLE III.

Observed and Computed Values of the Thomson Effect in Alloys.

Percentage of Tin in Alloy.	σ Observed.	σ Calculated.
1.00	−676	−111.3
2.00*	−537	− 68.3
3.72	−207	−141.9
6.36	−137	−135.5

* The thermoelectric powers were very different for the two specimens in this case.

differed considerably in their thermoelectric properties. It will be seen that the agreement is not all that could be desired. The Thomson effect is expressed in microvolts per degree Centigrade, and pure bismuth was taken as the standard substance and the observed value of its Thomson effect assumed correct.

[1] PHYS. REV., N. S., XII., pp. 231–237, Sept., 1918.

CONSTANTS OF ELECTRICAL CONDUCTIVITY.

According to the preceding paper

$$\rho_1/\rho_0 = e^{z(T_1-T_0)} \cdot (T_1/T_0)^{1/2}, \tag{29}$$

where ρ_1 and ρ_0 are the resistivities at T_1^0 and T_0^0 absolute, respectively, and z is a constant depending upon the metal, which we may call the conductivity constant. From the above equation we obtained

$$z = \log (1 + \beta) - \tfrac{1}{2} \log (1 + 1/T_0), \tag{29b}$$

where β is the temperature coefficient of resistance.

In Table IV. the values of z given in the third column were calculated

TABLE IV.

Coefficients of Resistance and the Conductivity Constant.

Temperature.	β Observed.	z.	β Calculated.
0° C.	.00427	.002423	.003917
15	401	2259	3821
20	393	2209	3791
25	385	2157	3763
30	378	2115	3735
50	352	1957	3633

from the data given in the first two columns, these data being given for 100 per cent. conductivity copper in Table 317, page 285 of the Smithsonian Physical Tables. In the fourth column this operation has been reversed and β has been calculated by assuming a value of z corresponding to about 35° C., namely, .00207. This value corresponds to the mean temperature of the table. Just as we see that the calculated values of z are not quite constant, so we see that the calculated values of β do not vary fast enough.

The first and second columns of Table V. also refer to 100 per cent. conductivity copper and were taken from Table 318, page 285 of the

TABLE V.

Variations of Resistance with Temperature, Observed and Calculated.

Temp. in ° C.	ρ_{20}/ρ_t from Tables.	ρ_t/ρ_{25} Calc. from Tables.	ρ_t/ρ_{25} Calc. from Eqn. (29).	Per Cent. Error.	ρ_t/ρ_{25} Calc. from $\rho \propto T$.	Per Cent. Error.
0	1.0853	.8727	.8757	+.35	.8864	+1.57
10	1.0409	.9083	.9101	+.20	.9189	+1.17
20	1.0000	.9442	.9451	+.10	.9513	+ .75
30	.9622	.9814	.9814	0	.9838	+ .24
40	.9271	1.0184	1.0184	0	1.0163	− .21
50	.8945	1.0559	1.0564	+.05	1.0487	− .68
60	.8642	1.0926	1.0950	+.22	1.0811	−1.05
70	.8358	1.1298	1.1345	+.35	1.1136	−1.43

Smithsonian Tables. The numbers in the third column were calculated from those in the second. The fourth column was obtained by starting with the correct value of the resistivity at 35° C., using $z = .00207$, and calculating the resistivity at other temperatures by means of equation (29). The percentage error in these calculated values is given in the fifth column. The sixth column was calculated from the empirical law that the resistance is proportional to the absolute temperature, and the seventh contains the corresponding percentage errors. The average error in the fifth column is .16 per cent., while that in the seventh is .89 per cent., or over five times as much. It will thus be seen that the

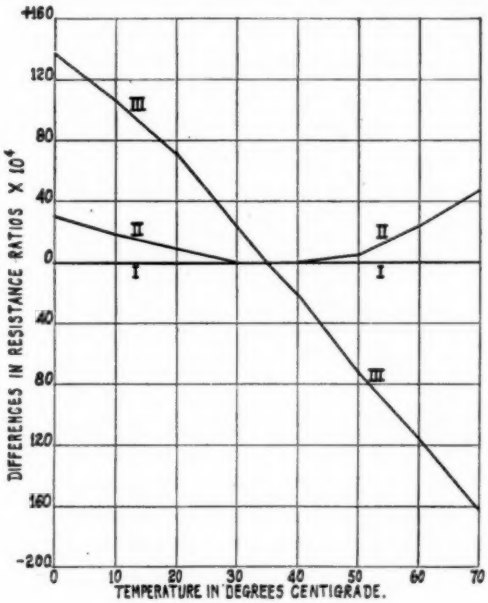


Fig. 1.

theoretical equation for electrical conductivity, or resistance, agrees with experiment much better than the empirical law. This fact is visualized in Fig. 1 in which the differences between the resistance ratios as given in the third, fourth and sixth columns of Table V. are plotted as ordinates, the experimental values given in the third column being taken as a basis, and the temperatures as abscissæ. Curve I. with the differences all zero therefore represents the data in the third column, Curve II. those in the fourth column and Curve III. those in the sixth column.

Table VI. is based on Table 308, page 276 of the Smithsonian Tables, columns 1, 2 and 3 being taken from the tables and columns 4, 5 and 6 being computed.

TABLE VI.

Conductivity Constants of a Number of Metals.

Substance.	Temp. °C.	β.	z.	Average z.	$z_1 - z_2$.
Aluminium	18–100	+.0039	+.0024		
"	25	34	17		
"	100	40	24		
"	500	50	43	+.0027	−.0001
Bismuth	0–100	458	30	.0030	+.0002
Cadmium	0–100	42	26	.0026	−.0002
Copper	0–50	(See Table IV.)		.0022	−.0006
"	100	.0038	.0024		
"	400	42	34		
"	1000	62	22	.0027	−.0001
Gold	18–100	368	216		
"	100	25	11		
"	500	35	28		
"	1000	49	45	.0026	−.0002
Iron, pure	18–100	62	46		
" "	25	52	35		
" "	100	68	54		
" "	500	147	140		
" " *	1000	50	46	.0044*	+.0016
Lead	18–100	43	28	.0028	0
Magnesium	0–100	38	22		
"	25	50	33		
"	100	45	31		
"	500	36	29		
"	600	100	94	.0029*	+.0001
Mercury	0–15	.00088	−.00094	−.00094	−.0037
Molybdenum	25	.0033	+.0016		
"	100	34	20		
"	500	50	43		
"	1000	48	44	+.0031	+.0003
Nickel	0–100	62	46		
"	25	43	26		
"	100	43	29		
"	500	30	23		
"	1000	37	30	.0031	+.0003
Palladium	0–100	35	19	.0019	−.0009
Platinum	0–100	37	21	.0021	−.0007
Silver	0–100	40	24		
"	25	30	13		
"	100	36	22		
"	500	44	37	.0024	−.0004
Steel, glass hardened	Assumed	16	+.00004	+.00004	−.00276
" , blue	to be at	33	175	.00175	−.00105
" , piano wire	50° C.	32	165	.00165	−.00115
Tantalum	0–100	33	17	.0017	−.0011
Tin	18–100	46	31	.0031	+.0003

Substance.	Temp. °C.	β.	x.	Average x.	x_1-x_2.
Tungsten	18–100	+.0045	+.0030		
"	500	57	50		
"	1000	89	85	+.0055	+.0027
Zinc	0–100	40	24	.0024	−.0004

* In each of these cases the exceptionally large value of x was omitted in taking the average.

From the ratio of the initial concentrations of the electrons in any two metals, a_1/a_2, given in Table I., and the values of x, the temperature coefficient of the concentration of the electrons, also given in Table I., it is possible to determine the relative concentrations of the electrons in different metals at any temperature. Similar information may be obtained for the positive centers provided we can determine the ratios of their initial concentrations, that is, b_1/b_2, and the corresponding values of y, the temperature coefficient of the concentration of the positive centers. We have so far been unable to determine the values of the ratio b_1/b_2, but if we assume the average value of the radii of the positive centers in one metal to be equal to the average value in another metal at the same temperature, then the ratio of the values of b, that is, b_1/b_2, will be equal to the reciprocal of the ratio c_1/c_2, which is the ratio of the initial mean free paths of the electrons in the same two metals. The ratio of the mean free paths of the electrons, λ_1/λ_2, at any temperature depends upon the value of the ratio c_1/c_2 and the values of y, the temperature coefficient of the concentration of the positive centers. For

$$\frac{c_1}{c_2} = \frac{\rho_2 a_2}{\rho_1 a_1} e^{(x_1-x_2)T}, \tag{30}$$

and

$$\frac{\lambda_1}{\lambda_2} = \frac{\rho_2 a_2}{\rho_1 a_1} e^{(x_2-x_1)T}, \tag{30a}$$

the latter equation being deduced from the former and equation (11), quoted at the beginning of this paper.

The data given in the first three columns of Table VII. were taken from Table 307, pages 274–276 of the Smithsonian Physical tables, the values of ρ, the specific resistance, given in the second column corresponding to the temperatures given in the third column. The values of the ratios of the specific resistances, ρ_1/ρ_2, given in the fourth column were calculated for the Centigrade zero with the aid of the temperature coefficients of resistance, β, quoted in column 3 of Table VI. In computing the ratios of the mean free paths at the absolute zero, c_1/c_2, and those at the Centigrade zero, λ_1/λ_2, given in the fifth and sixth columns

of Table VII., respectively, the values of ρ_1/ρ_2 were taken from the fourth column of this table, those of a_1/a_2, the initial concentration of the electrons, from the fifth column of Table I., and those of $(z_1 - z_2)$, the difference in the conductivity constants, from the sixth column of Table VI. The values of $(x_1 - x_2)$, the difference in the temperature coefficients of concentration of the electrons, were obtained from the sixth column of Table I. The values of y, the temperature coefficient of concentration of the positive centers, given in the seventh column of Table VII. were calculated by adding the values of x, the temperature

TABLE VII.

Mean Free Paths of the Electrons and Temperature Coefficients of Concentration of the Positive Centers.

Substance.	ρ.	Temp.	ρ_1/ρ_2.	c_1/c_2.	λ_1/λ_2.	y.
Aluminium	2.62	0° C.	.1284	7.43	7.53	.0045
Cadmium	7.54	18	.3415	2.49	2.30	40
Copper, unannealed	1.724	20	.0776	10.77	12.33	40
" , hard drawn	1.77	20	.0796	10.50	12.02	
Gold	2.42	18	.1108	8.55	8.73	44
Iron	8.85	0	.4340	4.83	3.64	68
Lead	20.4	0	1.0000	1.00	1.00	47
Magnesium	4.35	0	.2137	5.08	5.10	49
Nickel	6.93	0	.3396	2.91	3.15	56
Palladium	10.21	0	.5005	1.63	2.33	42
Platinum, hard	10.96	0	.537	1.62	2.01	41
" , malleable				1.58	1.98	
Silver	1.468	0	.0719	12.20	12.99	41
Steel, glass-hardened	45.7	0	2.241	.265	.62	23
" , blue	20.5	0	1.005	.942	1.39	40
" , piano wire	11.8	0	.5785	2.214	3.32	39
Tin	13.0	0	.6365	1.67	1.51	49
Zinc	5.75	0	.2818	3.01	3.11	40

coefficient of concentration of the electrons, given in the seventh column of Table I. to those of z, the conductivity constant, given in the fifth column of Table VI.

NUMBERS OF ELECTRONS AND POSITIVE CENTERS.

An examination of the values of the ratio N_1/N_2 shows that, if iron, nickel and palladium are excluded, the variations in the concentrations of the electrons in different metals at 0° C. do not exceed four per cent. of the mean value. In iron the ratio is 18 per cent. below the mean, while in nickel it is 29 per cent. above, and in palladium over seven per cent. above. If we exclude these metals and cadmium, we find that the values of the exponent x lie within a range of about twenty per cent.,

the average being in the neighborhood of .0018. The values of x for the first three metals are unusually large and that for cadmium small. It follows that as higher temperatures are reached the concentrations of electrons in nickel and palladium will exceed those in other metals more and more, while that in iron will gradually overtake and finally exceed that for most metals. The concentration in cadmium at high temperatures should fall short of that for other metals.

The concentrations of the positive centers vary within wide limits as is shown by the values of the ratio λ_1/λ_2, the values of this ratio ranging from .62 to 12.99. High values of the electrical resistance accompany small values of this ratio in practically every case. This would indicate that differences in electrical conductivity depend principally upon the concentrations of the positive centers, rather than upon that of the electrons. The variations in the concentrations of the positive centers with temperature are indicated by the values of y. Excluding iron, nickel and steel, these values lie between .0039 and .0049, most being in the neighborhood of .0040. The values for iron and nickel are high, while that for glass-hardened steel is quite small. Other kinds of steel fall in the group of well-behaved metals. Steel probably should be treated as an alloy, and as pointed out in the preceding paper, there are reasons for believing that the numbers of positive centers do not increase as rapidly in alloys as in pure metals. It looks as if both the concentrations of electrons and of positive centers in pure ferromagnetic substances increase faster than in other substances.

The values obtained for z at different temperatures for the same metal seem to indicate, as was suggested in the earlier paper, that the expressions involving electrical conductivity are not exact. The agreement is much better in the case of thermoelectricity.

PHYSICAL LABORATORY,
UNIVERSITY OF OREGON,
July, 1919.

THE MEASUREMENT OF VERY SHORT TIME INTERVALS.

BY PAUL E. KLOPSTEG.

SYNOPSIS.

Measurement of very short time intervals; a partial deflection method.—After briefly reviewing the usual method of determining time intervals of the order of microseconds, the author describes a method in which the potential difference of a condenser after it has been discharged for the interval of time to be measured, is accurately determined by connecting the condenser through a ballistic galvanometer to a known potential difference, which is made nearly the same as that to be measured, so that the small throw observed merely measures the small correction to be applied to the known potential difference to give the unknown. A steady current through a known resistance is used as the source of known potential difference. The arrangement of circuits is described and also a gang switch which simplifies the experimental manipulation and eliminates possible error from absorbed charge in the condenser. The working equation for computing the time interval from the observations shows that the attainable accuracy depends on the accuracy of a resistance, a resistance ratio and a capacity. The method was tested with the aid of a Helmholtz pendulum and it was shown that an interval of 250 microseconds may be measured with such *accuracy* that the probable error of each observation need not exceed 0.15 per cent. The *precision* was such as to enable the determination of an overall temperature coefficient of the Helmholtz pendulum and accessories amounting to about 1 microsecond per degree for the interval just mentioned.

Measurement of the rate of detonation of explosives; a source of error.—An attempt to apply the above method to measure the rate of detonation of dynamite and trinitrotoluol gave inconsistent results, probably because, on account of the intense ionization, the condenser continued to discharge through the gas after the wire was broken.

1. GENERAL.

NO particular novelty attaches to the determination of time intervals of the order of microseconds. A method for doing this, utilizing the partial discharge of a condenser through a resistance—both of known values—seems first to have been described by Sabine.[1] It was employed by Kennelly[2] in 1889, and later by various other investigators.[3] Briefly, the usual procedure is to measure the initial and remaining charges or potentials of the condenser, respectively, before and after the discharge

[1] Phil. Mag., 1 (5), 337, 1876.

[2] Reference in paper by Kennelly and Northrup, Jour. Frank. Inst., 172, 30, 1911.

[3] Radakovic, Wien. Akad. Ber., 109 (II.a), 276 and 941, 1900; Parker, PHYS. REV., 16, 243, 1903; Kozak, Mitteil. über Gegenst. d. Art.-u. Geniewes., 893, 1903 and 556, 1904; Edelmann, Phys. ZS., 5, 461, 1904; Devaux-Charbonnel, C. R., 142, 1080, 1906; Coulsen, PHYS. REV., 4, 40, 1914; Barnett, PHYS. REV., 12, 103, 1918. The method has also been used by A. G. Webster for a number of years.

has been allowed to proceed during the interval being measured. Then, from the usual relations

$$\tau = CR \log_e \frac{Q_0}{Q} \qquad (1a)$$

or

$$\tau = CR \log_e \frac{E_0}{E}, \qquad (1b)$$

the time is computed. To determine the charges represented in the first of these equations, a ballistic galvanometer is used. The potential differences represented in the second equation are obtained with an electrometer. The latter method is described in an unpublished paper by one of A. G. Webster's students. The writer is indebted to Dr. Webster for a copy of this paper.

A galvanometer is generally conceded to be a more workable instrument than an electrometer. In seeking to develop a method of this kind to give maximum accuracy with thorough convenience, one therefore turns to the former instrument as offering greater possibilities. From the standpoint of accuracy null methods or, if these are impracticable, partial deflection methods[1] of measurement are generally superior to total deflection methods. The application of eq. (1*a*) illustrates the latter method. Here we presuppose an unvarying source of potential difference charging the capacity C with a quantity Q_0. This total quantity, as well as the remaining quantity Q, are in turn discharged through the ballistic galvanometer, resulting in readings which are theoretically proportional to the respective quantities. Even with a calibrated scale, increasing the charging potential and therefore the throws, adds nothing to the probable percentage accuracy of the results, except with a very slow galvanometer, because of the increasing rapidity of reversal of the motion with increasing throws. In the total deflection method, also, one cannot assume strict proportionality of throws and quantities, because of non-uniformity of the galvanometer field;[2] and to maintain accuracy of results, frequent calibration is necessary.

In the measurement of capacities with a ballistic galvanometer, this difficulty was overcome by the method of mixtures, in which the unknown capacity and a known capacity neutralize each other's charges, more or less completely, and only the excess charge is passed through the galvanometer. Kennelly and Northrup, in the paper cited, applied this method to the determination of the remaining charge Q, after the fully charged condenser had discharged during the unknown interval.

[1] Of this principle the Brooks deflection potentiometer is an excellent illustration.

[2] PHYS. REV., 7, 637, 1916.

The work here described had been completed before the writer had learned of the work of Kennelly and Northrup. The application of the method of mixtures to the problem, as mentioned in the preceding paragraph, had been tried, but rejected, because the purpose of the work was to find a method which, if need should arise, might be used in the field as well as in the laboratory. The above method, because of the fact that two condensers of good quality and known capacity are needed, and because of the somewhat complicated circuits, did not seem to meet the requirements.

To secure the same advantage of small throws, and of making the accuracy of the measurement depend upon fixed quantities, preferably resistances and resistance ratios, another method of attack presented itself. This is to oppose, through a ballistic galvanometer, the remaining potential difference at the condenser terminals, after the partial discharge,

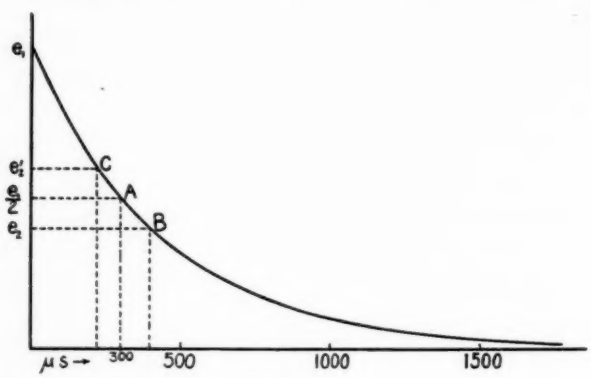


Fig. 1.

by an equal or almost equal *steady* potential difference. Then, if both the potential differences mentioned are equal, there will be zero galvanometer throw; but if the one or the other is greater, that across the condenser terminals will assume the value of the steady potential difference, the equalizing charge passing through the galvanometer, with a resulting small positive or negative throw. This idea forms the basis of the present method.

The discharge curve, Fig. 1, shows clearly what is involved. The curve represents clearly the relation between time and remaining potential difference across the condenser when the latter discharges through a pure resistance. Suppose the time interval during which the condenser discharges is of the order of 300 microseconds (300×10^{-6} sec.) and that the resistance through which the discharge takes place is of such value that the initial potential falls, in this interval, to exactly half value.

This is represented by point A on the curve. With the same capacity and resistance, but with a longer or shorter interval, the points B or C, respectively, might represent the final condition. In the first instance, no throw would result if the steady potential difference $e_1/2$ were thrown across the condenser terminals through the galvanometer; but in the second and third cases, a small throw would result, to the right or left, respectively. In the second case, the throw would correspond to a change of potential difference across the condenser from e_2 to $e_1/2$; and in the third case, the throw would represent the equalizing charge as the potential difference across the condenser changed from e_2' to $e_1/2$.

From what has been said, it is obvious that any partial deflection method of this kind requires approximate knowledge of the time interval to be measured. Otherwise it would be impossible to keep the galvanometer throws small, and the advantages of such a method would be lost. But in nearly any case which may arise one can, by computation or preliminary measurement, gain sufficient knowledge of the conditions of the experiment to enable the successful application of a partial deflection method.

2. Arrangement of Circuits.

Fig. 2 represents in diagram the apparatus for making determinations in the manner suggested. Let F_1 and F_2 represent two contacts which may be opened in such quick succession that the interval between breaks is of the desired magnitude. This may be accomplished with a Helmholtz pendulum,[1] or with a fall apparatus of a type as described by Hiecke[2] and Webster.[3] With the reversing switch R closed in position a, a fall of potential e_1 exists at the terminals of r_1, and e_2 at the terminals of r_2. Arbitrarily let $r_1 = 2r_2$, although any other ratio in which $r_1 > r_2$ would answer. These potential differences are proportional to the resistances, since the same steady current flows through both the latter. The condenser C is thus kept at a potential difference e_1 so long as F_1 remains closed. At the instant of opening F_1, however, the battery is cut off and the condenser discharges through r_1 until F_2 is opened.

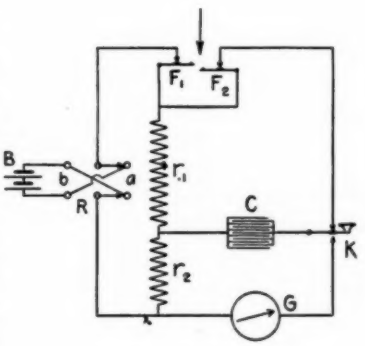


Fig. 2.

[1] Ann. d. Physik, 3, 274, 1900.

[2] Hiecke, Sitzber. d. k. Akad. d. Wiss. in Wien, Abt. IIa, 96, 114, 1887.

[3] Webster, Phys. Rev., O. S., 6, 297, 1898.

As stated before, if the resistance r_1, the capacity and the interval between breaks are properly related, the potential difference at the condenser terminals will now have become e_2, or half its original value. With resistances and capacity fixed, any deviation from the value e_2 is due to an actual interval different from the expected interval. The galvanometer throw is observed by first closing F_1—or, more conveniently, a switch in parallel with F_1—then reversing R, and finally depressing K. These operations have put a potential difference e_2 across r_2 in the proper direction to oppose the remaining potential difference across C, and have brought the latter to the value e_2 by means of the equalizing charge which has passed through the galvanometer.

3. Details of Apparatus.

In the apparatus as finally designed, all the operations necessary for observation of the galvanometer throw are accomplished with a single motion of a special gang switch. An additional feature of the switch is the provision which is made so that connection between condenser and galvanometer can persist for an instant only. In this manner only the "free charge"[1] or geometric capacity of the condenser is used, and errors which might otherwise arise from absorbed charge effects are eliminated.

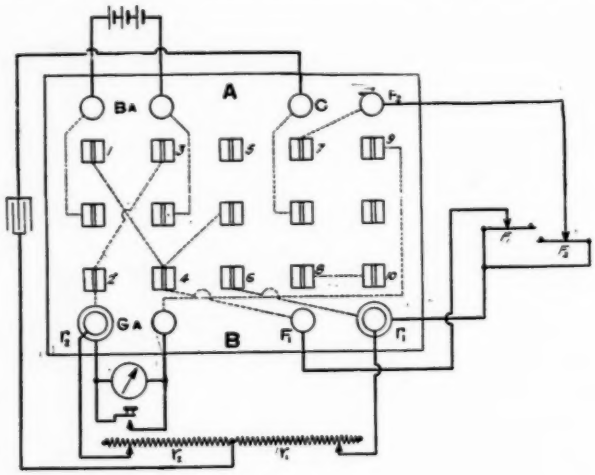


Fig. 3.

The arrangement of this gang switch is shown in Fig. 3, in which dotted lines represent internal, and solid lines external connections.

The switch is of the rocker or quick throw type, with the lengths of its blades so proportioned that the operations outlined in connection

[1] Zeleny, A., PHYS. REV., O. S., 22, 1906, 65.

with Fig. 2 take place in proper sequence as the switch is thrown from position "A" to position "B." Normally its position is "A," the blades engaging in the odd-numbered clips. With the switch in this position, the breaks at F_1 and F_2, which delimit the interval being measured, are made to occur. In throwing the switch, to obtain the galvanometer reading, the sequence of operations is as follows:

(1) Open at 7; disconnects condenser from charging source. (2) Close at 6; equivalent to closing F_1. (3) Open at 1 and 3, close at 2 and 4; reverses direction of fall of potential along r_2. (4) Close at 8 and 10; this opposes the fall of potential along r_2 to that across the condenser, through the galvanometer. During this operation 9 and 10 are bridged by the blade. (5) Open at 9. The combination of (4) and (5) keeps the condenser and galvanometer connected for a very brief interval only, as stated above. The switch is kept in position "B" until the reading has been taken.

4. Theoretical.

The reasoning which must be followed in order to obtain the equation upon which to base the measurements, and by which the observed values are reduced, is now evident. Upon the basis (1) of the known capacity, (2) of a predetermined ratio of initial to remaining potential difference at the condenser terminals, and (3) of the estimated interval, we must first determine the values of r_1 and r_2 so that, during the expected interval, the condenser shall discharge by an amount determined by the ratio. The equation giving the relations between these quantities will enable us to determine τ from the observations.

Let us suppose that the operations are carried out as previously described, and that a small galvanometer throw is observed, which may be positive or negative. The quantity producing this throw will have the value

$$\pm \Delta Q = \left(\frac{Q}{C} - e_2\right) C, \tag{2}$$

and the direction of its discharge depends upon the relative magnitudes of Q/C and e_2. In this equation Q, the remaining charge in the condenser has the value eC, where e is the remaining potential difference at the end of the interval τ. From (2) we obtain

$$Q = e_2 C \pm \Delta Q. \tag{3}$$

We know, according to equations (1) that

$$\tau = Cr_1 \log_e \frac{Q_0}{Q}, \tag{4}$$

and that the initial charge of the condenser

$$Q_0 = e_1 C. \tag{5}$$

If e_0 is the total fall of potential along r_1 and r_2 in series,

$$e_1 = e_0 \frac{r_1}{r_1 + r_2}, \tag{6}$$

and

$$e_2 = e_0 \frac{r_2}{r_1 + r_2}. \tag{7}$$

With proper substitutions of equations (3), (5), (6) and (7) in (4), we immediately have

$$\tau = C r_1 \log_e \frac{1}{\frac{r_2}{r_1} \pm \frac{\Delta Q}{e_0 C}\left(\frac{r_1 + r_2}{r_1}\right)}. \tag{8}$$

This equation enables us to determine the values of r_1 and r_2 to be used in the measurement; for we know that in the ideal case, when the estimated and actual intervals are equal, ΔQ is zero. To illustrate, let us suppose the interval to be 10^{-4} second, the ratio $r_1 : r_2 = 2 : 1$, and the capacity 1 microfarad. Then

$$r_1 = \frac{\tau}{C \log_e 2} = \frac{10^{-4}}{10^{-6} \cdot 0.6932},$$

or

$$r_1 = 144.3 \text{ ohms},$$

and

$$r_2 = 72.15 \text{ ohms}.$$

Equation (8), as it stands, cannot be used advantageously for obtaining τ from an observed throw corresponding to the discharge of the quantity ΔQ, for it would still involve obtaining the relatively very large throw resulting from the discharge of the quantity $e_0 C$ through the galvanometer. The requisite modification, which amounts to finding a ready means for determining the ballistic constant of the galvanometer, is readily made.

Suppose the potential difference across the condenser terminals to change by a small amount, from e_1' to e_2', and that the small quantity of electricity q, corresponding to this change, passes through the galvanometer. This condition is realized by choosing r_1' only slightly greater than r_2', their sum still remaining $r_1 + r_2$, as in the measurement, and throwing the gang switch from "A" to "B." We then have

$$\left.\begin{aligned} q &= (e_1' - e_2')C = i(r_1' - r_2')C, \\ \text{and} \quad e_0 C &= (e_1 + e_2)C = i(r_1 + r_2)C. \end{aligned}\right\} \tag{9}$$

Since i is the same in both cases, because of the equality of $r_1' + r_2'$

and $r_1 + r_2$, a steady battery being assumed,

$$\frac{r_1 + r_2}{e_0 C} = \frac{r_1' - r_2'}{q}. \tag{10}$$

By substituting this value of the left-hand member of the equation in eq. (8), putting for the small quantities of electricity involved the corresponding proportional throws of the galvanometer, and changing to common logarithms, we arrive at the working equation,

$$\tau = 2.303\, C r_1 \log \frac{1}{\frac{r_2}{r_1} \pm \frac{d_x}{d_0}\left(\frac{r_1' - r_2'}{r_1}\right)}. \tag{11}$$

In this equation d_x represents the throw corresponding to the quantity ΔQ, and d_0 the throw corresponding to q, or the calibrating throw. The positive sign is used when the throws are in the same direction, and negative when opposite.

The equation shows that the accuracy of measurement attainable depends chiefly upon the accuracy of the resistance values and of their ratio, and of the capacity value of the condenser. When the actual and estimated intervals differ by a small amount, as they usually will, the second term in the denominator in eq. (11) may be regarded as a correction to be applied to the ratio of the resistances.

The sensitivity of the method may be made very great by using a sensitive ballistic galvanometer and a sufficiently high source of potential difference. In the ordinary or total deflection method one is limited by the fact that only small quantities of electricity can be measured, even at a full scale throw of the galvanometer. The present method is equivalent to suppressing the origin of readings quite out of the range of the scale, or to securing a much magnified angle with strict proportionality of scale readings and quantity, together with ease of reading. The experiments made have indicated that with a properly constructed "absolute" fall apparatus of the Hiecke[1] or Webster[2] type, condenser capacities may be determined by this method with considerable accuracy.

5. Experimental.

As a means for investigating the possibilities of this method, a Helmholtz pendulum was kindly placed at the writer's disposal by the Bureau of Standards.[3] This instrument does not so readily lend itself to com-

[1] Loc. cit. [2] Loc. cit.

[3] The experiments were conducted in the Electrical Division of the Bureau. To the chief and the members of this division the writer expresses his thanks for their helpful interest, and for the use of equipment. In this connection he desires especially to mention Drs. W. F. G. Swann and P. G. Agnew.

putation of the intervals as do the fall devices of Hiecke and Webster; but its design and construction are of such excellence that its performance in accurately reproducing any given interval within its range left nothing to be desired. The electrical apparatus, represented in Fig. 3, consisted of Wolff resistance boxes, a Leeds and Northrup precision condenser and Type *R* galvanometer. The special gang switch was also constructed in the shops of the Leeds and Northrup Company.

The first step in the experiment was to find the relative positions of F_1 and F_2 on the Helmholtz pendulum for simultaneous breaks. F_1 was fixed in position so that it should be opened at the instant the pendulum passed through its lowermost position. F_2, on a micrometer slide, was set so that it should open slightly later than F_1. In eq. (11) one con-

TABLE I.

C = 1.000 microfarad, $r_1' = r_1$, $r_2' = r_2$, $r_2/r_1 = .4$, d_0 and d are single readings. Second column indicates number of complete turns of the micrometer head which shifts position of F_2. Scale distance, 60 cm. T = 21° C.

Obs. No.	No. Turns.	d_0, Cm.	d, Cm.	r_1.	r_2.	$t(\mu s)$.
a.....	1.000	12.24	−.04	175	70	161.2
b.....	2.000	12.27	−.02	350	140	321.5
c.....	2.000	12.27	+.21	360	144	321.6
d.....	3.000	12.29	−.04	525	210	483.7
e.....	3.000	12.32	+.13	535	214	482.1
f.....	3.000	12.33	+.26	545	218	482.5
g.....	3.000	12.31	−.31	505	202	482.6
h.....	4.000	12.33	−.05	700	280	646.0
i.....	5.000	12.32	−.03	875	350	805.1
j.....	5.000	12.34	+.58	950	380	805.8
k.....	5.000	12.32	−1.22	750	300	807.8
l.....	1.000	12.20	−.05	175	70	161.5
m[1].....	1.000	12.22	+.80	195	78	160.4

[1] Repetitions of obs. "a," turning micrometer back to original setting.

dition for $\tau = 0$, or simultaneous breaks, is that $r_1 = r_2$ simultaneously with $d_x = 0$. This was made the basis for the adjustment. With r_1 and r_2 equal, and connections as in Fig. 3, the pendulum was "dropped," and d_x observed. F_2 was then moved in small steps, so as to diminish the interval, until a zero throw was observed after dropping the pendulum and throwing the switch. The possibility was kept in mind that zero throw might be obtained in case F_2 should open before F_1. To check

this point, F_1 and F_2 were interchanged by means of a double throw switch, and the adjustment continued until for either connection the throw remained zero. The position of F_2 so determined was taken as the origin of readings for its adjusting micrometer.

The set of observations and results recorded in Table I., representing a calibration of the pendulum, is typical of the results attainable by this method. Where observations of the interval for a given setting of the micrometer were repeated, with different electrical constants, excellent agreement invariably resulted. It should be noted that any error in a result includes those of mechanical imperfections in the pendulum as well as those of electrical quantities. The close agreement indicates that both of these must be small.

In another series of observations, the question of reproducibility of a short interval was particularly considered. From the calibration of Table I., the micrometer setting corresponding to an interval of 250 microseconds was obtained. Keeping the contacts fixed for this interval, and using various combinations of capacity and resistance values, sets of ten readings with each particular combination were taken. The results are given in Table II.

In connection with Table II., two interesting things may be pointed out.

It seemed desirable to know the effect upon the value of τ computed by eq. (11) of an error in the observed throw d_x. The relation was found by the usual process of partial differentiation, assuming constant values for all quantities except for the ratio d_x/d_0, d_x being the variable, and for τ. The probable error in the mean of the ten observations and in the single determination of d_x, were used in the resulting expression to determine the corresponding probable errors in τ. Observation series *c* may be taken as illustrative of the entire group. Here it is found that the probable error in the mean τ is .04 per cent., and in the individual observation, .13 per cent. The values in the last column of Table II., which are computed from the mean value of d_x, are therefore probably correct to 0.2 microsecond or better, as indicated.

The question at once arises as to the reason for the differences of several microseconds in the different values of the last column, since the settings of the pendulum contacts were fixed. Consideration of this question leads to the second interesting point.

It should be noticed first that the electrical constants were the same in series *c*, *e* and *f* only, so that the differences in these three cases cannot be ascribed to different probable errors in the values of the electrical constants. We should, upon first thought, expect closer agreement, because the values should be relatively correct, apart from the question

TABLE II.

Obs. No.	Temp.	Cap M. F.	r_1'.	r_2'.	d_0.	r_1.	r_2.	d_x.		t (μs).
a, 1–17–'18, a.m...	20°	1.0002	275	265	1.58	360	180	−.23	−.23	
								.23	.26	
								.25	.23	252.6±.1
								.25	.26	
								.23	.23	
b, 1–17–'18, p.m...	21°	1.0002	201	191	2.16	280	112	+.37	+.26	
								.37	.29	
								.40	.33	253.2±.2
								.29	.32	
								.30	.31	
c, 1–17–'18, p.m...	21°	0.5006	560	520	1.58	720	360	−.14	−.18	
								.15	.16	
								.17	.17	253.8±.1
								.16	.15	
								.15	.14	
d, 1–18–'18, a.m...	15°.6	0.5006	395	375	1.12	550	220	+.20	+.18	
								.19	.18	
								.20	.18	248.1±.1
								.21	.17	
								.18	.18	
e, 1–18–'18, a.m...	15°.8	0.5006	560	20	1.58	720	360	+.05	+.02	
								.05	.08	
								.03	.06	248.5±.2
								.09	.05	
								.05	.06	
f, 1–18–'18, p.m...	19°	0.5006	560	520	1.59	720	360	−.05	−.06	
								.09	.06	
								.06	.05	251.3±.2
								.06	.04	
								.08	.04	

of their correctness in absolute values. However, it is seen in the column of temperatures, observations "*d*" were made on a fuel-saving day, on which the temperature in the laboratory was 5.4° cooler than on the preceding day, when observations "*c*" were obtained. An obvious conclusion is that the apparatus had a temperature coefficient. This coefficient turns out to be + 1.05 microsecond per degree. Accordingly, the result at 19° should be 251.7 microseconds. The actual result found in series "*f*" was 251.3. Numerous other experiments, the results of which are not here tabulated, as well as those recorded in Table II., are in agreement with the conclusion stated.

Making proper allowance for the temperature coefficient, and taking into account the probable errors in the values of the capacities and resistances used, the discrepancies become very small, and we find that the method, with simple means, gives results considerably more accurate than can be expected from total deflection methods unless extreme precautions are used. We also find that the Helmholtz pendulum is capable of reproducing the very short time intervals in a manner which, when we consider the factors involved, must be called surprising. In intervals as small as 10 microseconds, an overall accuracy of two per cent. was easily attainable.

6. Applications.

The necessity for making measurements of intervals of the magnitude here dealt with arises in certain kinds of investigations, as is seen from the list of papers cited at the beginning of this article.

By the method here described, velocities of high power rifle bullets, as high as 900 meters per second, have been successfully determined between two points 20 cm. apart. It should be understood, however, that for routine field testing of ammunition, other methods are more adaptable since operators with little skill and training are able by them to make determinations more successfully than by a method involving the use of a galvanometer. In velocity measurements, the greatest errors are likely to arise from lack of sharpness or preciseness of the breaks produced by the projectile. They are mechanical errors, rather than errors in the electrical quantities. This question, because of other urgent work, could not be investigated in great detail. Preliminary work showed that glass-hard drill rod, or silvered glass strip, or mercury in capillary glass tubes should prove superior to ordinary wires for preciseness of the breaks.

The failure of the method in an attempted application to determining the detonation rates of dynamite and trinitrotoluol had its cause in an interesting phenomenon. The apparatus was set up as in Fig. 3, and wires were drawn through the stick of dynamite, at two points 100 cm. apart, to provide for the necessary breaks. All circuits were very carefully insulated, so that no leakage errors could occur from this source. With supposedly uniform explosives—the rate of detonation of which is of the order of 5,000 meters per second—the results varied by as much as five per cent. These variations were found to be probably due to the intense ionization produced by the explosion which causes leakage between the broken ends of the wires, and thus causes deviations from the theoretical value in the discharge rate of the condenser.

ISENTROPIC COEFFICIENT OF EXPANSION.[1]

BY SATYENDRA RAY.

SYNOPSIS.

Isentropic coefficient of expansion.—The square root of the ratio of the specific heat to the isopiestic coefficient of expansion of a substance, has the dimensions of a velocity. The ratio of this quantity to the velocity of sound in the substance is therefore a pure number which is proved by the author to be equal to $\sqrt{(-\theta\alpha_\phi)}$, where α_ϕ is the isentropic coefficient of expansion. If we call the quantity in brackets k, then *for gases*, $k = 1/(\gamma - 1)$ where γ is the ratio of the specific heats. *For liquids*, k is found to be approximately equal to unity, which means that $\alpha_\phi = -1/\theta$, a law analogous to Charles' law for gases. *For solids*, k varies from about 0.3 to 1. It is seen that as any substance passes from the gaseous through the liquid to the solid state, k decreases from more than 1 to less than 1. The significance of this fact with reference to the theory of corresponding states is briefly discussed.

Thermodynamic equations for the expansion of liquids and solids.—The author shows that the *generalized adibaatic equation for any substance* is $v\theta^k$ = constant, and he derives the following *general expansion law for any substance*, an extension of the general gas law: $pv = ms_p/\theta\beta_v(\alpha_p - \alpha_\phi)$, where $\beta = dp/pd\theta$.

IT is worth our while to examine the dimensional aspects of expressions and equations in heat as carefully as they are examined in electricity and magnetism. For example take the three equations of heat,

$$dv = \alpha v d\theta \qquad \text{from thermometry.}$$

$$dQ = msd\theta \qquad \text{from calorimetry.}$$

$$dQ = kA\frac{d\theta}{dx}\cdot dt \qquad \text{from conductivity.}$$

Obviously α, s, and k are not constants, for if they were we would get three different dimensions for θ from the three equations that are inconsistent with one another.

Assuming then α, s, k and θ all to have dimensions—to be different "things," that is—instead of being pure numbers, we have the three dimensional relations following (it being remembered that heat is expressed in "ergs," heat being of the nature of energy):

$$[L^3] = [\alpha L^3\theta] \qquad \text{or} \qquad [\alpha] = \left[\frac{1}{\theta}\right],$$

$$\left[M\frac{L^2}{T^2}\right] = [Ms\theta] \qquad \text{or} \qquad [s] = \left[\frac{L^2}{\theta T^2}\right],$$

$$\left[M\frac{L^2}{T^2}\right] = \left[kL^2\frac{\theta}{L}\cdot T\right] \qquad \text{or} \qquad [k] = \left[\frac{ML}{\theta T^3}\right].$$

[1] Read at the Science Congress, Calcutta, March 2, 1919.

We note, whatever α, s and θ may be,

$$\sqrt{\frac{s}{\alpha}} = \frac{L}{T} \text{ (a velocity)},$$

The question is what is it the velocity of? s and α are heat coefficients and it might be the velocity of a heat wave, but the value obtained comes nearer the velocity of sound. The following tables gives a comparison between $\sqrt{s/\alpha}$ and velocity of sound as experimentally determined.

Solids

	Al.	Au.	Co.	Cu.	Fe.	Pb.	Ni.	Pt.	Ag.	Sn.	Zn.	Units.
$\sqrt{s/\alpha}$	34	17.5	34.2	28	40	12.4	34.5	23	20	19	22.2	10^4 cm./sec.
v	51	20	47	40	40	12.3	50	27	26	25	37	"

Liquids *Gases*

	Water.	Alcohol.	Ether.	Turpentine.	Petroleum.	Air.	H_2.	O_2.	N_2O.	NH_3.	CO_2.	Units.
$\sqrt{s/\alpha}$	14.6	15.1	12	13.7	14.7	5.26	19.7	5.3	4.6	7.5	4.6	10^4 cm./sec.
v	14.3	12.6	11.4	13.7	14	3.3	12.9	3.17	2.6	4.2	2.6	"

We notice (1) that $\sqrt{s/\alpha}$ is comparable with the velocity of sound and (2) that in the case of solids the calculated values are as a general rule too small, for liquids about right or slightly greater, and in gases much greater still.

A small part of the difference is due to the variation of s, α, and v with temperature. Perhaps if we could get corresponding values we might get closer agreement between $\sqrt{s/\alpha}$ and v. The probability of $\sqrt{s/\alpha}$ accidentally coming of the same order in the 22 cases calculated is very small. Also the changing of the sign of the error with the change of state is explicable from theory if we could make it independently establish the formula as in the light wave. A friend suggests that the heat wave of which $\sqrt{s/\alpha}$ is the expression is the adiabatic wave, which is identical with the sound disturbance.

Examining for identity of expression $\sqrt{s/\alpha}$ with the well-known expression $\sqrt{E_\phi/\rho}$ we have,

$$\sqrt{\frac{E_\phi}{\rho}} = \sqrt{\frac{-v\left(\frac{dp}{dv}\right)_\phi}{\frac{m}{v}}}$$

$$= \sqrt{-\frac{v}{m} \cdot \frac{\left(\frac{dp}{d\theta}\right)_\phi}{\frac{1}{v} \cdot \left(\frac{dv}{d\theta}\right)_\phi}}$$

$$= \sqrt{-\frac{v}{m} \cdot \frac{\left(\frac{d\varphi}{dv}\right)_p}{\alpha_\phi}} \qquad \text{where } \alpha_\phi = \frac{1}{v} \cdot \left(\frac{dv}{d\theta}\right)_\phi$$

$$= \sqrt{-\frac{1}{\theta\alpha_\phi} \cdot \frac{\frac{1}{m} \cdot \left(\frac{dQ}{d\theta}\right)_p}{\frac{1}{v} \cdot \left(\frac{dv}{d\theta}\right)_p}}$$

$$= \sqrt{-\frac{1}{\theta\alpha_\phi}} \cdot \sqrt{\frac{s_p}{\alpha_p}}. \qquad \text{(I.)}$$

This is a perfectly general relation. The velocity is $\sqrt{s/\alpha}$ multiplied by a factor $\sqrt{-(1/\theta\alpha_\phi)}$. Examining it dimensionally we notice it is pure number as θ and α_ϕ are dimensionally inverse of one another.

This factor is practically equal to unity in the case of liquids; which means that for them

$$\alpha_\phi = -\frac{1}{\theta}. \qquad \text{(II.)}$$

In words, entropy remaining constant, the volume of a liquid decreases by 1/273 of its volume at 0° C. for one degree rise of temperature,—a Charles's Law Analogue for liquids.

The deviation of $\sqrt{s/\alpha}$ from the experimental value of the velocity enables us to calculate this isentropic coefficient of expansion for solids and gases. Putting

$$\alpha_\phi = -\frac{k}{\theta}$$

we see k is less than unity for solids and greater than it for gases. The smallest value of k in the cases calculated in the table is 0.36, whilst for gases it is 4 and may be 10 or more for a very complex molecule. We might call k the coefficient of aggregation, the value changing from solid to the gaseous state with the aggregation of molecule and passing through the value of unity in the liquid condition. k for gases can be easily seen to have the value

$$\frac{s_v}{s_p - s_v} \qquad \text{and} \qquad \alpha_\phi = -\frac{s_v}{s_p - s_v} \cdot \frac{1}{\theta},$$

a value which when substituted in (I.) gives close agreement with the experimental value of v for gases.

Value of k thus calculated gives us the equation of the adiabatic corresponding to any substance. For if

$$\frac{1}{v}\cdot\left(\frac{dv}{d\theta}\right)_\phi = -\frac{k}{\theta},$$

$$v\theta^k = \text{const.} \qquad \text{(III.)}$$

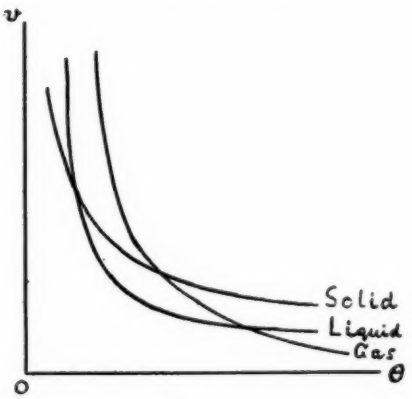


Fig. 1.

The nature of the θ, v graph for the three states is indicated in the diagram. The θ, v equation for the adiabatic for gases reduces to the form

$$v\theta^{s_v/R} = \frac{1}{R^{s_v/R}}\cdot e^{\phi/R},$$

exponent of θ being the coefficient of aggregation for the gas.

A general relation between the isopiestic and isentropic coefficients of expansion can be easily established. We have,

$$\left(\frac{dp}{d\theta}\right)_\phi\cdot\left(\frac{dv}{d\varphi}\right)_\theta - \left(\frac{dp}{d\varphi}\right)_\theta\cdot\left(\frac{dv}{d\theta}\right)_\phi = 1;$$

$$\therefore\ \frac{1}{v}\cdot\left(\frac{dv}{d\theta}\right)_\phi = \frac{1}{v}\cdot\left(\frac{dv}{d\theta}\right)_p\left\{1 - \left(\frac{d\varphi}{dv}\right)_p\cdot\left(\frac{d\theta}{dp}\right)_v\right\}$$

or

$$\alpha_\phi = \alpha_p\left\{1 - \left(\frac{d\varphi}{dv}\right)_p\cdot\left(\frac{d\theta}{dp}\right)_v\right\}, \qquad \text{(IV.)}$$

k and consequently α_ϕ being known, (IV.) would give us a relation between $(d\varphi/dv)_p$ and $(d\theta/dp)_v$ or what is the same thing between $(d\theta/dp)_\phi$ and $(d\theta/dp)_v$.

Thus

$$\left(1 - \frac{\alpha_\phi}{\alpha_p}\right) = \left(\frac{d\varphi}{dv}\right)_p\cdot\left(\frac{d\theta}{dp}\right)_v$$

or

$$\frac{1}{\theta}\cdot\left(\frac{dQ}{dv}\right)_p = \left(\frac{\alpha_p - \alpha_\phi}{\alpha_p}\right)\cdot\left(\frac{dp}{d\theta}\right)_v,$$

whence

$$S_p = \frac{\theta}{m} \cdot \left(\frac{\alpha_p - \alpha_\phi}{\alpha_p} \right) \cdot \alpha_p \beta_v \cdot pv \qquad \text{(V.)}$$

β_v being put for $\frac{1}{p} \cdot \left(\frac{dp}{d\theta} \right)_v$.

This is Boyle's law analogue for solids and liquids and may be thrown in the form

$$pv = m \frac{S_p}{\theta(\alpha_p - \alpha_\phi)\beta_v} \qquad \text{(Va)}$$

and it reduces to the form $pv = mR\theta$, for gases, as can easily be seen.

For agreement with the results of actual gases, Van der Waals' generalization alters the left-hand member of the formula for the ideal gas. The thermodynamic relations show we can extend the application of the formula for ideal gases to matter in general by altering the value of R in the right-hand member, keeping the left-hand member intact. In equation (V., *a*), it must be remembered none of the coefficients involved are constants, and that we have to take the instantaneous and simultaneous values of all the terms involved.

The relation between $(d\theta/dp)_\phi$ and $(d\theta/dp)_v$ is best remembered through the coefficient of pressure

From (IV.)

$$\left(\frac{dp}{d\theta} \right)_\phi = \left(\frac{d\varphi}{dv} \right)_p = \left(\frac{\alpha_p - \alpha_\theta}{\alpha_p} \right) \cdot \left(\frac{dp}{d\theta} \right)_v$$

or

$$\beta_\phi = \left(\frac{\alpha_p - \alpha_\phi}{\alpha_p} \right) \cdot \beta_v. \qquad \text{(VI.)}$$

For gases,

$$\alpha_p = \beta_v;$$

$$\therefore \quad \alpha_p = \alpha_\phi + B_\phi$$

or

$$\frac{\beta_\phi}{\alpha_\phi} = -\gamma.$$

Returning to the expression $\sqrt{E_\phi/\rho}$ we find

$$E_\phi = -\frac{\beta_\phi}{\alpha_\phi} \cdot p$$

and

$$\sqrt{\frac{E_\phi}{\rho}} = \sqrt{\frac{(\theta\alpha_p + k)}{k\alpha_p} \cdot \frac{\beta_v}{\rho}}. \qquad \text{(VII.)}$$

We note (1) that α_ϕ is different in value from the isopiestic coefficient, as indeed it must be, (2) that it is invariably negative in sign, as a reference to the isentropic for gases would make perfectly obvious, (3) that the equality of coefficient, noted for the isopiestic coefficient in the case of

gases, is transferred to the liquid condition, (4) that the range through which the coefficient varies for different substances gets distinctly shortened, k lying somewhere between 0.36 and 4 when α_p ranges from .0036 to .000027 for the 22 cases given in the tables.

Referring to Carnot's cycle we get one little feature regarding it.

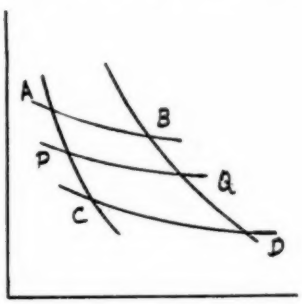


Fig. 2.

θ being the absolute temperature and the coefficient of expansion being $-(k/\theta)$ it means that the corresponding points like P, Q on the adiabatic the working substance is contracting at the same rate, a rate *inversely* proportional to the absolute temperature at the instant, exactly as along the isothermal it absorbs heat *directly* proportional to the absolute temperature.

This isentropic coefficient of expansion is moreover a brick in the bridge of continuity of state. As the same substance exists in the 3 states at different temperatures we see the value of the isentropic coefficient $-(k/\theta)$ is changing with temperature, k passing through the value of unity somewhere in the liquid condition during a continuous change from the solid to the gaseous state.

The value $k = 1$, which is a geometric mean of sorts between the highest and lowest values of k, defines a state of aggregation for us which might be called the ideal liquid condition and the temperature at which $k = 1$, may be called the temperature of transit.

This temperature would be analogous to the critical temperature, in its position in the theory of continuity of state, but whereas the critical temperature spans only two states, solid-liquid or liquid-gas, the temperature of transit would span all the three conditions together. If k change by jumps from its maximum value to its minimum, the value nearest to unity may be chosen. It appears k has an important place in the kinetic theory of matter and we may call it the coefficient of aggregation, as it depends upon and settles the state of aggregation of the molecules of a body.

LUCKNOW, INDIA.

RADIATION PRODUCED BY PARTIAL IONIZATION.

BY C. D. CHILD.

SYNOPSIS.

Emission of light by gases; a partial ionization theory.—In certain cases light seems to be emitted at the instant of ionization of the gas atoms; in other cases it seems to be emitted at the instant of recombination of gas ions; and in still other cases, the light emission seems to be associated with neither ionization nor recombination. These cases are discussed and an explanation is suggested which is based on Bohr's assumption that radiation occurs when an electron falls from an outer to an inner orbit, combined with the assumption that complete ionization is produced much less frequently than partial ionization, that is, the displacement of an electron from an orbit to one farther out. Partial ionization would not affect the current or the electric field, so its existence cannot be directly proved but is rendered probable by the recent demonstration of radiation without ionization. The readjustment following it may be expected to produce radiation similar to that produced by recombination after complete ionization. The evidence given by canal rays is briefly discussed. The author's theory apparently explains all the phenomena cited.

Low-voltage discharge in Hg vapor.—If a Wehnelt cathode is used, a low-voltage discharge may be maintained which is relatively non-luminous for some distance from the cathode.

THERE are many reasons for believing that a gaseous body radiates energy when it is ionized. It is not, however, certain whether radiation occurs at the time when the atoms are ionized, or when the ions recombine. Indeed certain facts appear to indicate that the radiation is not produced by either ionization nor recombination. The following is a discussion of these facts and a suggestion that at least the phenomena pertaining to monatomic gases may be explained, if we assume that radiation is indeed caused by the recombination of parts of atoms, but that in the majority of cases the recombination takes place between parts of an atom that have been only partially separated from each other, the electron falling back to the same nucleus as that to which it was originally attached. Many of the phenomena of gases which are not monatomic can, no doubt, be explained in the same way, but since these are more complicated, they will not be discussed at this time.

Phenomena Indicating that Radiation is Due to Recombination.—In the discussion of the atom given by Bohr it is assumed that radiation occurs when an electron falls from an outer to an inner orbit, that is, radiation is produced when recombination occurs. Whether we accept this par-

ticular view of the atom or not, it is reasonable to expect that radiation will occur at such a time, for the sum of the potential and kinetic energies of the system decreases when the electron combines with a positive ion, and it is natural to suppose that the energy thus lost to the system is radiated.

Moreover, there is experimental evidence that in certain cases radiation is produced by a recombination of ions as has been shown by the experiments on the light emitted by the vapor above the mercury arc[1] and by the fact that light is emitted from a mercury arc for a brief time after the current has ceased.[2] Apparently there is no way of explaining either of these phenomena except by assuming that the light is produced at the time of recombination.

Phenomena Indicating that Radiation is Due to Ionization.—On the other hand certain phenomena are more easily explained by assuming that the light is emitted at the time of ionization. The following is an example of such phenomena. If electrical discharge is passed from a hot calcium oxide cathode, C (Fig. 1), to a mercury anode, A, through mercury vapor, it is possible to adjust the conditions so that there will be a glow at g with no light that can be observed between C and g. There is then a very definite line of demarkation between the nonluminous and the luminous regions. The luminous part is in fact the same as the first striation of an ordinary striated discharge, except that in the case here described there is no glow in the immediate neighborhood of the cathode.

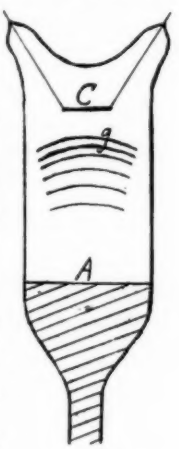


Fig. 1.

This glow shows approximately the same spectrum as that shown by the light radiated from the vapor above the mercury arc and yet it appears where we would expect ionization to occur and not where we would expect the greater part of the recombination. The electrons emitted from the cathode will not ionize in the immediate neighborhood of the cathode. In order to ionize they must first pass through a definite potential difference and this required voltage no doubt exists between C and the region in which the glow commences.

On the other hand the number of recombinations between g and C must be large. This number varies as the product of the number of the positive ions and of the electrons. The positive ions move toward C and hence are more numerous near C than near A. Since the electrons

[1] Phil. Mag. (6), 26, 906, 1913.
[2] PHYS. REV. (2), 9, 1, 1917.

come from C, there must also be a large number of electrons there. As a result there is a large number of recombinations near C.

In any case it is difficult to see how the number recombining can suddenly increase at a definite region. We, therefore, have good reason for believing that the light appears where the ionization and not where the recombination occurs. It is natural to draw the conclusion from this that the light is produced at the time of ionization rather than at the time of recombination.

While this appearance may be obtained with different conditions, a typical case is the following. The tube was 2.8 cm. in diameter. The distance from C to A was 3 cm. A was a mercury anode. The pressure of the gas as measured by a McLeod gauge was .002 mm. The tube was heated to approximately 80° C. The discharge was principally through mercury vapor as was shown by its spectrum. The potential difference between A and C was 16 volts. The current was .6 milliampere. In order to obtain the glow without light between C and g, it was usually necessary to raise the voltage slightly above 16 volts until the discharge became luminous and then gradually lower it until the region between C and g ceased to be luminous.

An attempt was made to measure the potential at g by inserting a platinum wire at that point. The potential difference between C and g as thus indicated was about 2 volts. It is probable, however, that the excess of electrons in this region and their high velocity give to the exploring wire a negative charge, so that its potential is below that of the region about it. The result would be to make this measurement of no value.

When the pressure of the mercury vapor was raised by allowing a slight amount of air to leak into the pump a higher voltage was required between C and A. However, when the voltage was so regulated as to bring the head of the striation to some fixed point the current between C and A and also the apparent voltage between C and g was always approximately the same provided the temperature of C was kept constant.

A similar result is shown when a stream of electrons (a cathode ray) or of positive ions (a canal ray) passes through a gas. As far as can be determined, the luminosity is limited to the region traversed by the moving particles. This is what would be expected, if the light is caused at the moment of ionization, for the ionization takes place in the path of the particles. It would not be expected, if the light were produced by recombination, for the recombination occurs not only where there is ionization, but also in the neighboring region to which the ions diffuse.

Phenomena Indicating that Light is due neither to Ionization nor to

Recombination.—There are other phenomena which seem to show that light is due neither to ionization nor to recombination. One of these is the fact that the amount of light emitted by a gas through which electrical discharge is passing is approximately proportional to the current flowing through the gas. It has been shown by the writer[1] that if the light were due to recombination of ions, it should vary approximately as the square of the current, since the number of recombinations varies as the product of the number of positive and of negative ions and each of these varies as the current.

Moreover the number of atoms ionized must be the same as the number recombining and, therefore, the number of atoms ionized varies approximately as the square of the current. If the light were due to ionization instead of recombination, it would still vary as the square of the current. Since the light does not in reality thus vary, it apparently is not caused by either ionization or recombination.

In the article to which reference has been given the writer made an attempt to reconcile these facts with the idea that the light is produced by recombination of the ions, but the work which has since been done on the elastic impact between electrons and the atoms of certain gases has made that attempt appear unreasonable as far as the discharge through such gases as mercury is concerned and improbable in all cases. Consequently if we accept the view that radiation is produced by either ionization or recombination, some explanation of this difficulty must be found.

Again when certain substances, as for example copper salts, are introduced into a non-luminous flame, it is possible to produce a line spectrum without any corresponding increase in the conductivity of the flame. That is we have radiation without ionization or recombination.

In the preceeding we have discussed the occurrence of light which is apparently not produced by either ionization or recombination. There is also one instance recorded in which there is apparently an abundance of ionization and recombination without any light. Graham[2] states that a current of 7 milliamperes was passed through a tube containing pure nitrogen at a pressure of 4 mm. without producing any light except in the immediate neighborhood of the electrodes, while with lower pressures a large amount of light was produced. We would certainly expect as much ionization with the higher pressures as with the lower, so that it would appear that here was an example of ionization and recombination without any resulting light.

[1] Phil. Mag. (6), 27, 278, 1914.

[2] Wied. Ann., 64, 49, 1898.

An Explanation of these Phenomena.—We have in the preceding paragraphs described two experiments which apparently show that radiation is due to recombination, two showing that it is due to ionization, and several showing that it is due neither to ionization nor recombination. It can, however, be shown that the suggestion made at the beginning of this article will explain these apparent contradictions. The assumption of Bohr and others that there is radiation whenever an electron falls from an outer to an inner orbit is there accepted, but to this is added the assumption that in the majority of cases of electrical discharge the electron falling from one orbit to another has never been entirely separated from its nucleus. It has received a shock which has driven it from its normal position, but not entirely away from the influence of the atom to which it belonged, so that it falls back to the same nucleus. Neither ionization nor recombination in the proper sense has occurred. It is rather partial ionization with a consequent return of the electron to its original position. Such an action would produce light, but would have no effect on the number of free ions. Neither the current nor the electric field would be influenced by such an occurrence.

There is the same effect, if the electron impinging on the atom is caught by the nucleus from which it has displaced an electron, so that there is merely an interchange of electrons without any increase in the number of those that are free.

It may first of all be noticed that such an incomplete ionization is what we should expect to occur in many, if not in the majority of cases. It requires more energy to separate an electron to a great distance than to remove it from an inner to an outer orbit. This is shown experimentally by the work of Davis and Goucher[1] and others on the voltage required to produce the single-lined spectrum. It is natural to expect that even a many-lined spectrum may be produced more easily than complete ionization. If such a difference exists, even though it is but small, many atoms will be hit by electrons which have attained sufficient velocity to displace an electron belonging to the atom to a considerable distance from its nucleus and will still not have sufficient velocity to ionize the atom completely. There will thus be many cases of incomplete ionization.

Such an assumption of course explains the appearance of light in the vapor above the mercury arc and of the continuance of light after the current has ceased, since in these cases we have recombination of the most complete type.

It explains the experiment in which light does not appear at the

[1] PHYS. REV. (2), 10, 101, 1917.

cathode, but begins at a definite region a few millimeters from it, namely at a point where ionization occurs and not in the region where the greatest recombination might be expected. We have no means of determining in this case the exact number of recombinations between completely separated ions, but it is probably much smaller than the number necessary to produce light that can be seen by the eye. This is probable since there are few positive ions present with which the electrons can combine. With non-luminous discharge the voltage is below that which is required to ionize the gas. When the discharge becomes luminous there is still no large increase in the current. This shows that with the current here used there is little ionization of the gas and consequently few positive ions present.

On the other hand the number of partial ionizations is probably much larger. Since the voltage is high enough to produce some complete ionization, it is probable that nearly every electron leaving the cathode produces either partial or complete ionization in this region. The number of recombinations of both the complete and the partial ionizations are sufficient to produce a visible amount of light. Since the recombination of the partially ionized atoms occurs where the ionization takes place and are thus concentrated to a greater extent it is not surprising the former should produce light while the later does not.

A similar explanation would account for the fact that the light produced by a stream of electrons or of positive ions is limited to the path of the ions.

The assumption made in the preceding explains the fact that the amount of light given by the mercury arc and other form of discharge is proportional to the current and not to the square of the current. While the number of recombinations resulting from complete ionization depends on the product of the number of positive and of negative ions and is consequently proportional to the square of the number of electrons present, the number of partial ionizations depends only on the number of electrons present and consequently is proportional to the first power of this number. Since the current is proportional to the number of electrons present (providing the electrical force is constant) the number of partial ionizations must be proportional to the current. The number of recombinations resulting from partial ionizations must be equal to the number of partial ionizations. If finally the light is proportional to such recombinations, it must also be proportional to the current, which is approximately what is found to occur.

This, of course, requires us to assume that nearly all of the light comes from partial ionizations, that is, that the number of partial ionizations is much larger than the number of complete ionizations. While we

might not have anticipated this conclusion, it is not unreasonable to accept it, if by so doing one can explain the phenomena here considered.

Again such an assumption explains the occurrence of a line spectrum when certain salts are introduced into a non-luminous flame even though there is no increase in the conductivity. As the single-lined spectrum of mercury may be produced without producing ionization, so the thermal or chemical action of the flame may be sufficient to displace an electron from an inner orbit to one further out without producing complete ionization.

In regard to the experiment of Graham's the explanation is not so evident. While several explanations might be suggested, one can not at present be certain that any of them is correct. In all probability the recombinations between completely ionized atoms taken alone were too small to produce a visible amount of light. Whether partial ionization was absent or whether it occurred under conditions such that no radiation in the visible spectrum occurred can not be stated. Certainly change in the density of a gas often produces large changes in the character of the spectrum. Until there has been further investigation of this phenomenon it is unwise to attempt any explanation. It would also be unwise at present to consider this as a proof that any large amount of ionization may occur without the production of radiation.

Evidence given by Canal Rays.—One might expect that decisive evidence regarding this subject would be given by a study of canal rays, but unfortunately those who have experimented most with these rays have failed to reach any agreement as to what they prove. Since there is this disagreement, the writer ventures to give the following reasons for believing that the light given by the canal rays which shows the Doppler effect is produced by recombination.

The following facts have a bearing on this discussion. First, when the light produced by the canal rays is properly examined the lines of the line spectrum of hydrogen and many lines of other gases are split into two parts, one being displaced and showing the Doppler effect, and one part being unaffected, there being a region of minimum intensity between the two parts.

Second, in order to have any luminosity in the region through which the rays are passing there must be some gas in that region.[1]

Third, the carrier of the displaced lines are the positive ions of the canal rays (the hitting atoms). Possibly the best proof for this is given by the spectrograms shown by Fulcher.[2] Thus spectrogram No. 160 shows that when hydrogen canal rays bombard air molecules, the dis-

[1] Fulcher, Astrophys. Jour., 33, 31, 1911.

[2] Astro-phys. Jour., 35, 103, 1912.

placed line of hydrogen alone is obtained. This would seem to be clear evidence that the light showing the Doppler effect is emitted by the hitting atoms.

Further the vibration which produces the light can not be started at the time the ion is produced. First because if it were so started, it would be necessary for it to continue until a high velocity were attained. Otherwise it would show no Doppler effect. If it were thus started and continued, we should have the greatest amount of light emitted when the ion was first agitated, that is, when the ion had a small velocity and the light would gradually fade out as the velocity was increased. This would produce an undisplaced line in the spectrum together with a displaced part of less intensity with no minimum between the parts.

Secondly if the vibration were started at the time of ionization, the light given by the canal rays would be quite independent of the presence of any molecules aside from the positive ions (that is the hitting ions). As has been stated the opposite of this has been observed by Fulcher.

We are apparently compelled to accept the view that the carrier of the displaced lines are the hitting ions and that these ions are set in vibration after they have acquired a high velocity. This agitation might be due to an impact which would leave the ion charged positively, or to a recombination with an electron which would leave it uncharged. There is apparently no proof as to which of these is the correct explanation, but since the latter supposition is more in harmony with all the other phenomena which are known, it is but reasonable to accept it as the correct one. We conclude, therefore, that the evidence thus far given by the canal rays is in harmony with the view that light is produced by recombination.

Spectra taken under Different Conditions.—According to this explanation there should be a difference between the spectrum of light produced by the recombination of completely ionized atoms and that resulting from partial ionization. Such a difference is found to exist. The spectrum of the vapor arising from the mercury arc, where there is recombination between completely separated ions, is slightly different from that of the mercury arc where there is partial ionization. The two spectra show approximately the same lines but the relative intensity of the lines is different, so that the light from the vapor about the arc is yellower than that of the arc itself.

The greater part of this article was written while the writer was at Cornell University. He, therefore, desires to express his thanks to Professor Nichols and to the members of the physics department of Cornell University for the privileges which were granted him while there.

COLGATE UNIVERSITY, September, 1919

SOME STUDIES OF METALS BY MEANS OF X-RAYS.

BY S. NISHIKAWA AND G. ASAHARA.

SYNOPSIS.

X-ray patterns of metals; (1) *effect of rolling.*—By passing a narrow beam of heterogeneous rays through a thin sheet of metal, a pattern may be photographically recorded which depends on the crystalline structure of the metal. The authors have used this phenomenon to study the effect of rolling and subsequent annealing on various metals. (*a*) In the case of *aluminum, cadmium, copper, zinc,* and *brass,* rolling produced ill-defined patterns, all with a symmetry related to the direction of rolling but each characteristic of a particular metal. (*b*) *Silver* and *tin* gave similar ill-defined patterns immediately after rolling, but these gradually changed during the following two or three weeks to the distinct spot patterns characteristic of annealed samples. For these metals, then, the crystal growth which accompanies annealing takes place at room temperatures. Even at 5° the recovery from rolling goes on, though more slowly (See Plate I). (*c*) *Lead* and *thallium* gave irregularly distributed spots which showed no symmetry related to the direction of rolling. For these metals, then, either the crystal structure is not distorted by the rolling or the recovery is quite rapid. In the case of thallium, however, the pattern was not the same as after the sheet had been annealed. (2) *The effect of annealing after rolling* was studied with a special furnace which enabled the patterns to be obtained for a sheet of metal kept at any desired temperature up to 800°. The various metals differ greatly in their response to annealing. Thirty minutes at 80° is sufficient to obliterate the effects of rolling in the case of *silver* and *tin,* whereas 2 hours at 800° is not sufficient for *copper.* The effects of annealing *cadmium* at 100°, 150°, 200° and 250° are shown in the photographs reproduced in Plate II. This method should be very valuable for studying the effect on metals of various mechanical and heat treatments.

Transformation point of thallium and tin as determined by X-ray patterns.—When the pattern produced by a thin sheet of annealed *thallium* was photographed for a series of ascending temperatures, it was found that as the transformation point was passed, the pattern suddenly changed to one corresponding to a single crystal. On cooling the sheet, the change was reversed (See Plate III). Taking account of the lag, the temperature of transformation was found to be about 227°, in good agreement with determinations by other methods. *Tin* was also investigated in this way, especially in the neighborhood of 160°, but no change of pattern was observed.

THE patterns obtained by passing X-rays through metals have been studied by several authors.[1] As some of these investigators pointed out, the patterns seem to depend to a great extent on the history

[1] W. Friedrich, Phys. Zeitsch., 14, p. 317, 1913.
E. Hupka, Phys. Zeitsch., 14, p. 623, 1913.
H. B. Keene, Nature, 91, p. 607, 1913.
S. Nishikawa and S. Ono, Proc. Tokio math. Phys. Soc., Ser. 2, 7, p. 131, 1913.
P. Knipping, Phys. Zeitsch., 14, p. 996, 1913.
E. A. Owen and G. G. Blake, Nature, 92, p. 686, 1914.
K. E. F. Schmidt, Phys. Zeitsch., 17, p. 554, 1916.

of metals, *e.g.*, mechanical and heat treatment, etc. Although the theory has not been fully worked out, it seems to us that this method of studying metals may find an important application in physical metallurgy.

In the present experiments, we studied (I.) the effect of heat-treatment on the strain produced in metals by mechanical working; and (II.) the condition of metals at higher temperatures.

Part I. The Effect of Heat-Treatment on the Strain Produced in Metals by Mechanical Working.

Experimental Arrangements.—As the kind of mechanical working we resorted to rolling, for it gives a strain possessing a definite direction, which can be advantageously studied, and at the same time it may serve as a means of preparing the thin sheets of metal necessary for the transmission of X-rays.

The metals studied are: aluminium, cadmium, copper, lead, silver, thallium, tin, zinc and several kinds of brass.

The metals were cast in each case to a size of 30 mm. × 30 mm. × 4 mm. The ingots were then rolled to a thickness varying from 0.1 mm. to 0.18 mm. (0.54 mm. for aluminium). Some samples rolled directly from commercial products were also examined.

The photographs were taken by the ordinary transmission method using heterogeneous X-rays from a Coolidge tube, the maximum voltage applied being about 60,000 V. The distance between the sample and the photographic plate was 5 cm. and the diameter of the pencil of rays was 3 mm. The time of an exposure was one hour with a current of 5 milliamperes. More than one hundred photographs were taken of the various samples.

Experimental Results.—Rolled samples produce, in general, ill-defined patterns with a symmetry related to the direction of rolling. The patterns are, however, characteristic of each metal. For example, cf. No. 47 (Ag) and No. 27 (Sn), Plate I.[1]

Lead and thallium gave irregularly distributed spots instead of ill-defined patterns possessing a direction of symmetry. This will be expected, however, when we take into consideration the quick annealing effect even at room temperature.

To study the annealing effect on the rolled samples at different temperatures, the samples were heated for 30 minutes in each case in an electric furnace, or, for lower temperatures in an oil bath.

A marked change in the pattern is observed when a sample is annealed,

[1] The photographs reproduced in the plates are so arranged that the direction of rolling is vertical.

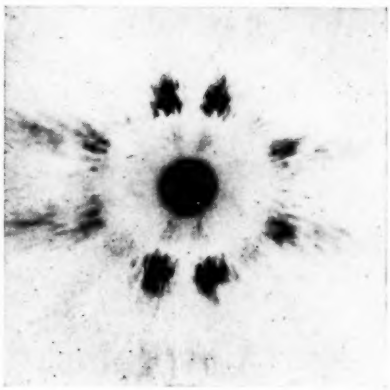
the amount of the change depending on the annealing temperature. A number of scattered spots appear, due to the growth of crystals, in place of the ill-defined patches given by rolled samples. Example: Cadmium, Nos. 34, 38, 60, 37, and 43, Plate II. The spots develop in size with the temperature and usually appear irregularly so that the direction of rolling can no longer be determined. In certain metals, however, the symmetry showing direction of rolling still remains even after a considerable annealing, *e.g.*, the direction of rolling was still to be observed in the case of copper even after it had been annealed at 800° C. for 2 hours. See No. 18, Plate II.

Silver and tin were found to give very markedly changed patterns after the rolled samples had been stored for some length of time even at low temperatures. In the case of tin, the photograph taken on the day following the rolling already displayed many spots, which means that the growth of minute crystals starts even at room temperature. Cf. No. 104, Plate I. Several photographs were taken at intervals in the course of three weeks and show a continual growth of crystals. A photograph given by a sample of tin stored at room temperature (about 23° C.) for 18 days has as many spots as that of the sample annealed at over 100° C. for 30 minutes. This indicates the entire removal of strain. Cf. No. 27′, Plate I. This sample had given the photograph No. 27, when exposed immediately after rolling. Samples stored at a temperature of about 5° C. were also tried and the change was found to be considerably slower. The spots, however, were perceptible in a photograph taken after one week. Cf. No. 110, Plate I. A sample of silver, which had given figure No. 47, Plate I, when exposed immediately after rolling, gave a pattern as shown by No. 109, Plate I, when the exposure was made after three weeks. The pattern is similar to those given by annealed samples of silver. This shows that the recrystallization occurred at room temperature.

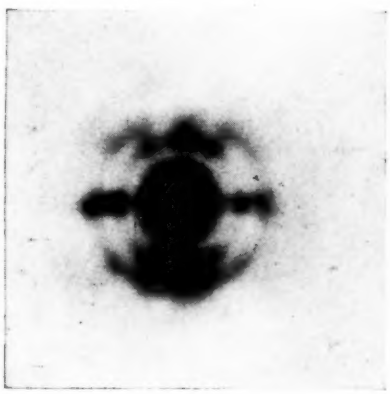
As it seemed interesting to study alloys as well as pure metals by this method, six samples of brass of various compositions (0–40 per cent. Zn) were prepared for examination.

As rolled, the pattern produced by brass with 2 per cent. of zinc differs slightly from that of pure copper. The patterns of brasses with 10 per cent., 30 per cent., and 35 per cent. of zinc are similar to one another but different from that of copper, while brass with 40 per cent. of zinc gives a distinctly different pattern. It is of interest to note that the above mentioned difference seems to be more pronounced when the patterns of the annealed samples are examined. The limit of the α solid solution of copper and zinc lies at about 37 per cent. of zinc, and brass containing

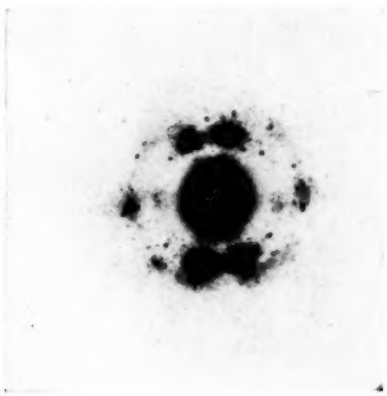
No. 47. Silver. Immediately after rolling.



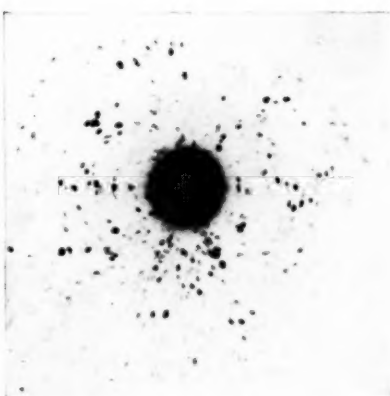
No. 109. Silver. Stored at room temperature for three weeks.



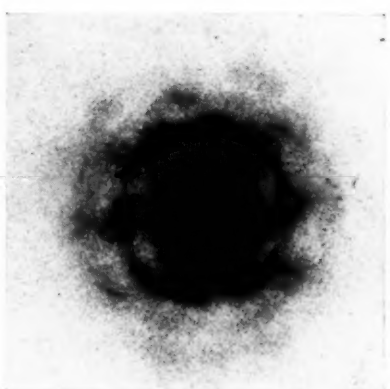
No. 27. Tin Immediately after rolling.



No. 104. Tin. Stored at room temperature for one day.



No. 27′. Tin. Stored at room temperature for 18 days.



No. 110. Tin. Stored at about 5° C. for one week.

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40 per cent. of zinc consists of α and β solid solutions. The present result is in accordance with this hypothesis.

Part II.

The X-ray method affords a serviceable means of studying metals at higher temperatures since the taking of photographs is not hindered, from the nature of the method, by any elevation of the temperature of the sample. This seems to be a merit when some other metallographical methods fail.

To study a sample in the heated condition, we constructed an apparatus which consisted of a small electric furnace contained in an evacuated cylindrical case. The cylinder is a brass tube (5 cm. diameter and 15 cm. long) closed at both ends. It has two glass windows which face the two open ends of the furnace inside so as to let X-rays pass through and to make the collimation possible. The small furnace, composed of a clay tube, 1 cm. diameter and 2 cm. in length, and a coil of fine nickel wire as its resistor, was heated by the current from a battery of secondary cells, so that steady supply of heat might be secured. The furnace was covered with a few layers of asbestos sheets. A calibrated thermojunction was placed close to the wall and at the center of the furnace. The leads for the heating current and the thermojunction wires, properly insulated, were introduced through brass tubes projecting from the upper cover of the cylinder. Air-tight sealing was effected at the terminals of these tubes so as to minimize the softening of the sealing material, the tubes serving as radiators. One remaining tube, communicating with the cylinder, was connected to an air pump and the cylinder was evacuated during the heating experiments.

A metal sample in the form of a thin sheet is mounted in a ring or short cylinder made of sheet copper and placed in the furnace so that it rests on the protected hot-end of the junction, due care being taken to minimize the difference in temperature between the sample and the junction. After the sample is put in the right position, the back window of the cylinder, through which the sample was introduced, is closed with a glass plate, a ring of rubber greased with vaseline serving as an air-tight washer. The temperature was read by means of a potentiometer and a mirror galvanometer. By employing a heating current from a set of secondary batteries and a suitable arrangement of resistances, the temperature could be regulated to within one tenth of a degree. During an experiment, X-rays pass through the front window of the cylinder, are transmitted through the sample held in the furnace, pass through the back window of the cylinder, and fall on the photographic plate,

which is about 4.5 cm. away from the sample. A good vacuum is maintained during the experiment so as to avoid oxidation of the sample. The time for one exposure was 30 minutes with a current of 5.5 milliamperes, other experimental arrangements being the same as those already described.

We have studied (*a*) the transformation in thallium[1] and (*b*) the effect of the time of annealing on the recrystallization of tin.

(*a*) *Transformation in Thallium.*—The sample of thallium used was from a rod made by Kahlbaum which had been rolled to a sheet about 0.1 mm. thick. The sample was heated up to a certain temperature and then cooled down, thus making a cycle. In some cases, more than one cycle was made with the same sample during a single experiment. Exposures were usually made while the sample was kept at constant temperature, but were sometimes made while the sample was gradually heated up or cooled down at a certain rate.

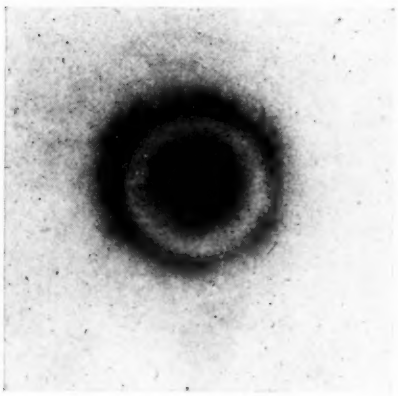
Several samples from the same piece of sheet thallium were studied in a series of experiments.

Samples as rolled invariably gave similar patterns a cluster of small spots radially arranged. (Cf. E 1, Plate III.)[2] This kind of pattern persists without change up to higher temperatures (cf. E 2, Plate III.), when it changes suddenly at a certain temperature to an entirely different kind of pattern with a set of spots just as in the case of a single crystal (cf. E 3, Plate III.). Once this change occurs, the new kind of pattern is retained when the temperature is further elevated (cf. E 4, Plate III.). This sudden change in pattern is observed again when exposures are made during the cooling trip of a temperature cycle (cf. E 5, Plate III.). Again, the new pattern is retained to room temperature (cf. E 6, Plate III.). In this case, the original kind of pattern with a cluster of spots radially arranged is not regained but another new type of pattern composed of a group of irregularly shaped spots is usually obtained. Sometimes a pattern with sets of well-defined spots appears instead, but even in these cases there is no question of the distinction between this pattern and the pattern belonging to the higher temperature.

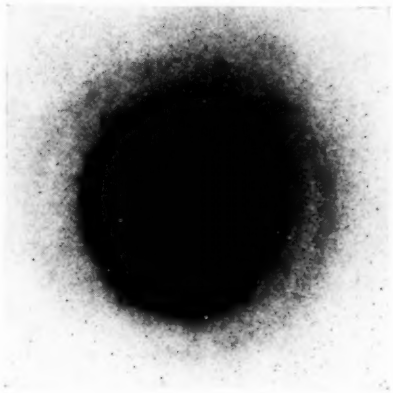
When repeating cycles of heatings and coolings with the same sample, we invariably get these abrupt changes in a series of photographs both on the heating and the cooling trips. Thus, in general, the abrupt change

[1] The transformation in borazite was studied using X-rays by H. Haga and F. M. Jaeger (Proc. K. Akad. Amsterdam, 16, p. 792, 1916). Recently A. J. Bijl and N. H. Kolkmeijer investigated the transformation of gray and white tin (Proc. K. Akad. Amsterdam, 21, p. 405, 1919).

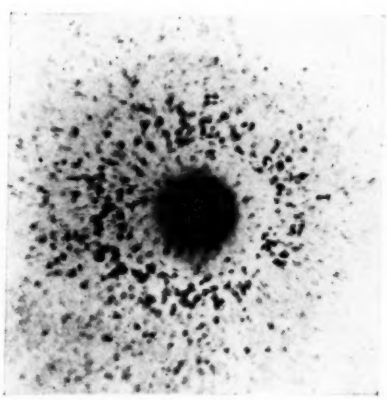
[2] The photographs, E 1 to E 6, which are reproduced as an example, were taken in series in a cycle.



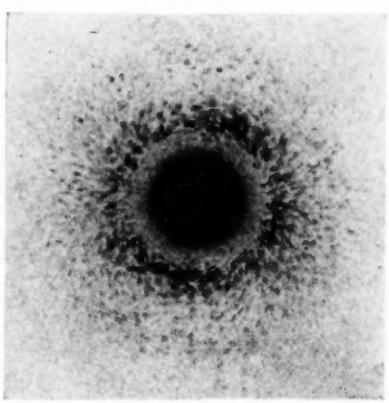
No. 34. Cadmium. Immediately after rolling.



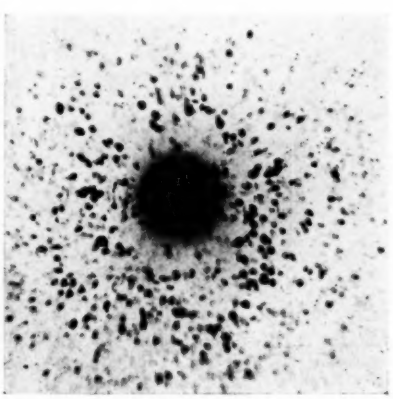
No. 38. Cadmium. Annealed at 100° C. for 30 minutes.



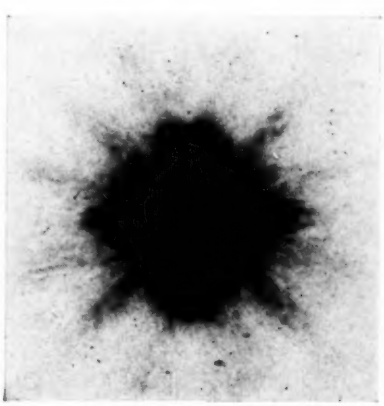
No. 60, Cadmium. Annealed at 150° C for 30 minutes.



No. 37. Cadmium. Annealed at 200° C. for 30 minutes.



No. 43. Cadmium. Annealed at 250° C. for 30 minutes.



No. 18. Copper. Annealed at 800° C. for two hours.

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of pattern divides a series of photographs in two. This fact shows very clearly that there exist two enantiomorphous modifications of thallium and that the transformation from one form to the other occurs during the temperature interval under consideration. The difference between patterns corresponding to the higher and lower temperatures is so marked that it is by no means to be mistaken for, or attributed to, an effect merely due to change in temperature.

In some exposures, during which the temperature of the sample was continually raised or lowered, the transformation temperature was crossed and photographs bearing at the same time both classes of pattern on one plate were obtained. Knowing the temperature interval during one exposure (30 min.) and changing the temperature at a constant rate, we can estimate approximately the temperature at which transformation occurred by comparing the intensities of the spots of both classes of pattern appearing on one and the same plate.

In our experiments we have found that the transformation always occurred a little higher on heating and a little lower on cooling, *i.e.*, there was a lag in the transformation. The lag seems to vary according to the rate of heating or cooling and to the degree of heat-treatment which had already been given to the sample. The lag is diminished on repeated cycles.

We have found, on summarizing several series of experiments, that the transformation in thallium occurs between 225° C. and 235° C., and is not far from 227° C., according to our estimation.

Rather discordant data are given by various investigators:

Transformation Temperature.	Method.	Authorities.
225 ° C.	Thermal analysis	Levin: Zeit. anorg. Chem., 45, p. 31, 1905.
225 ° C.	" "	Williams: Zeit. anorg. Chem., 50, p. 127, 1906.
227 ° C.	" "	Petrenko: Zeit. anorg. Chem., 50, p. 133, 1906.
231.8° C.	" "	Chikashige: Zeit. anorg. Chem., 51, p. 328, 1906.
227 ° C.	" "	Kurnakow and Puschin: Zeit. anorg. Chem., 52, p. 430, 1907.
230.5° C.	" "	Lewkonja: Zeit. anorg. Chem., 52, p. 452, 1907.
224 ° C.	" "	Dónski: Zeit. anorg. Chem., 57, p. 49, 1908.
238 ° C.	" "	Voss: Zeit. anorg. Chem., 57, p. 185, 1908.
226 ° C.	Viscosity (Flow Method) Elect. Conductivity. Thermoelectromotive-force	Werner: Zeit. anorg. Chem., 83, p. 275, 1913.

The present method seems to afford as accurate a means of determining the temperature of transformation as the other methods do. A more accurate determination may be made when the lag is minimized by an appropriate arrangement.

(*b*) The effect of the time of annealing on the recrystallization in rolled metals was studied in the case of tin.

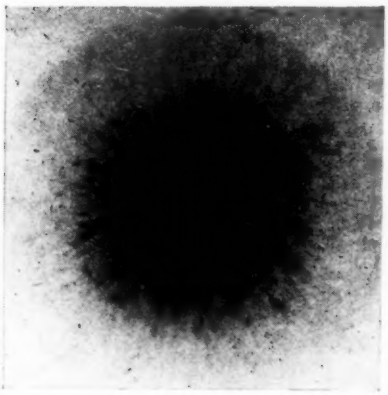
In one experiment, a sample of tin was heated up to 200° C., in 30 minutes, while the exposure was made. The sample was held at this temperature for hours, during which period several exposures (30 min. each) were made. A careful study of the photographs in the series revealed that the unit crystals had nearly attained their greatest size as soon as the sample reached this temperature, and very little development or change in pattern was observed between the pattern obtained in the 30 minutes immediately following the attainment of the temperature of 200° C. and that taken after an annealing for five hours at this temperature. The photographs taken at intervals during this period were also identical.

The plate, exposed while the sample was being heated from room temperature up to 200° C., showed that the characteristic ring pattern of rolled tin was being replaced by a pattern of spots.

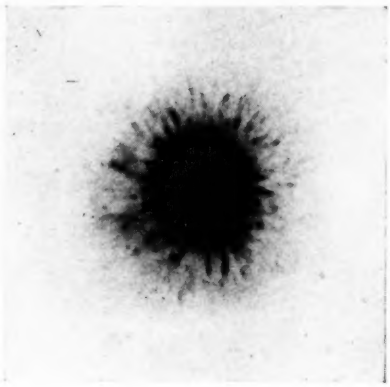
After about five hours' annealing at 200° C., the sample was cooled down to 170° C. in about 15 minutes, kept at that temperature for about 15 minutes and then the exposure was made while the temperature of the sample remained at 170° C. The sample was cooled down step by step in a similar manner and exposures were made at 160° C., 150° C., and 140° C. An additional exposure was made after the sample had been cooled down to room temperature. These photographs were all identical with the former ones.

Another similar experiment was tried at the temperature of 80° C. and we obtained a similar result, *i.e.*, the photographs taken at intervals in the course of three hours after the attainment of the maximum temperature do not vary from each other and the spots assumed an apparent maximum size, while the photograph taken during heating up to 80° C. shows the transitional period to this apparent maximum.

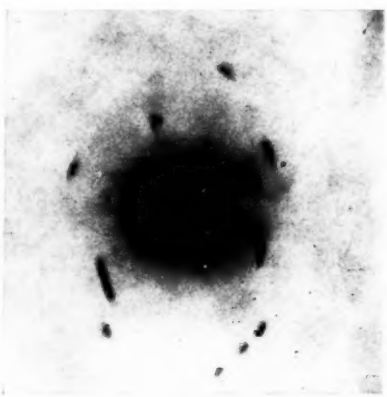
According to the present experiments, the apparent maximum growth of the unit crystals of tin is reached at an early stage in the annealing, even at a temperature of 80° C. Thirty minutes was found to be sufficient to reach this maximum. Further annealing does not result in a greater growth of the crystals. It is still open to question whether there is ever an ultimate or real maximum reached at the end of a sufficiently long annealing.



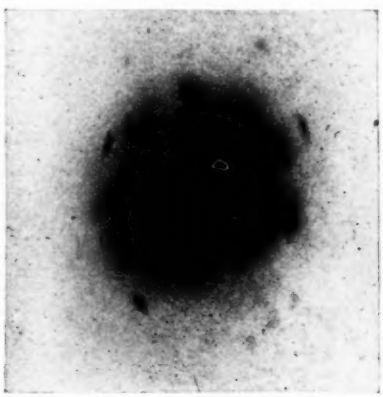
E 1. Thallium. At room temperature. As rolled.



E 2. Thallium. At 215° C. (on heating trip) (below transformation temperature).

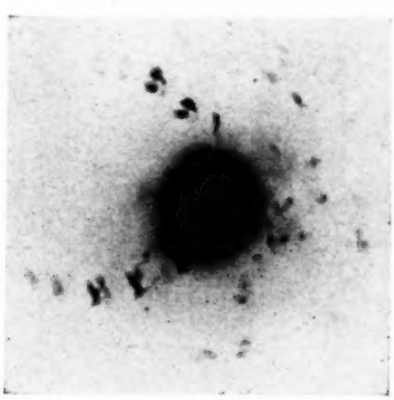


E 3. Thallium. At 235° C. (on heating trip) (above transformation temperature).



E 4. Thallium. At 245° C. (on heating trip) (above transformation temperature).

E 5. Thallium. At 235° C. (on cooling trip) (below transformation temperature).



E 6. Thallium. At room temperature (end of the cycle).

Incidentally, we could not observe the transformation in tin at about 160° C., as is claimed by certain investigators, though we made several experiments in this respect. This supposed transformation is rarely observed as shown by the literature. Whether this transformation does not really exist or is observable only under some conditions as yet undefined was not determined.

Our thanks are due to Professor E. L. Nichols for his encouragement and continued interest throughout the course of the experiments. We also wish to thank the staff of the laboratory for showing us every courtesy during the time we spent here.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY,
August, 1919.

[1] Tammann, Drudes Ann. Phys., 10, p. 647, 1903.
[2] Cohen, Zeit. phys. Chem., 50, p. 225, 1905.
[3] Degens, Zeit. anorg. Chem., 63, p. 207, 1909.
[4] Werner, Zeit. anorg. Chem., 83, p. 275, 1913.

A NEW METHOD OF DETERMINING THE TEMPERATURE VARIATION OF THE THERMAL CONDUCTIVITY. OF GASES. I.

BY G. H. HENDERSON.

SYNOPSIS.

Thermal conductivity of gases.—A new method of measuring the temperature variation of the thermal conductivity of a gas, by determining the temperature distribution in the gas contained between parallel plates maintained at different fixed temperatures, is described, and also a series of experiments made with air to test the method for temperature differences up to 500°. It was found that when the difference of temperature is not more than 100°, fairly accurate measurements may be made; but the larger the temperature difference, the more difficult it becomes to determine the temperature of the gas because of the large error due to radiation from the plates. If a thermo-element is used, as was done by the author, the error cannot be accurately computed because of the irregularities in the shape of the junction, hence the readings give only upper limits of the temperature coefficient. It is suggested that the temperatures might be measured with a fine wire resistance thermometer, but this was not tried. The disturbing effects due to convection may be made negligible.

Thermal conductivity of air.—The temperature coefficient between 20° and 500° was determined for air at atmospheric pressure, using the author's method. The temperature distribution was measured between an upper plate heated electrically and a lower water-cooled plate, by means of a small movable thermo-element. Because the large radiation corrections could not be determined accurately, the results for the higher temperatures can be considered only upper limits, but indicate that between 250° and 500°, the variation of the conductivity with the temperature is approximately linear. With an upper temperature of 100°, however, the results are more reliable and give a value for the coefficient (.00261) which is in good agreement with the results of other observers.

INTRODUCTION.

FROM a knowledge of the temperature gradient existing in a gas contained between two parallel planes maintained at different fixed temperatures, information may be derived concerning the thermal conductivity of the gas. As far as the writer is aware, no account of an investigation of such gradients has been published, except by Lasareff.[1] In Lasareff's experiments, gases at low pressures under gradients of only a few degrees per centimeter were investigated with the object of demonstrating the existence of a temperature discontinuity at the boundaries. In the present experiments the intention was to investigate steep temperature gradients in air at athospheric pressure, with the object of deter-

[1] Lasareff, P., Ann. der Phys., 37, p. 232, 1912.

mining the temperature variation of the thermal conductivity of air over a wide range of temperature. The present experimental evidence regarding the variation of thermal conductivity with temperature leaves much to be desired. Investigation has been largely confined to the region 0° to 100° C., and the results of various experimenters differ very widely.

If two infinite parallel planes are maintained at different fixed temperatures, the quantity of heat, Q, crossing unit area of any intermediate plane per second, is constant when a state of steady flow of heat is reached and is given by

$$Q = K\partial\theta/\partial z, \tag{1}$$

where K is the thermal conductivity of the gas and $\partial\theta/\partial z$ is the temperature gradient, z being the height above the lower plane.

The temperature gradient was obtained by noting temperatures at known points between the planes. The quantity Q was more difficult to measure with accuracy and hence absolute values of the conductivity were not sought for. However it seemed that relative values of K might be found from a knowledge of $\partial\theta/\partial z$ alone.

If we assume the variation of the thermal conductivity of air with the temperature, θ, to be given by

$$K = K_0(1 + \alpha\theta), \tag{2}$$

where K_0 is the thermal conductivity of air at the zero temperature and α may be called the temperature coefficient of thermal conductivity, then from (1) we obtain by integration

$$K_0(\theta + \tfrac{1}{2}\alpha\theta^2) = Qz. \tag{3}$$

On the other hand, if we assume the variation of thermal conductivity with the absolute temperature T to be given by

$$K = K_0T^n/T_0^n, \tag{4}$$

where n is a numerical constant, we have from (1)

$$z \propto T^{n+1}. \tag{5}$$

APPARATUS.

The apparatus used is shown in Fig. 1. It consisted of an upper hot plate and a lower cold plate between which air was enclosed by means of a glass ring. Temperatures in the air were measured by means of a thermocouple whose height was determined by means of a cathetometer.

The top plate was heated by an electric hot plate which was built up of sheets of asbestos slate as shown in Fig. 1. Coils of nichrome wire of No. 16 B. and S. gauge formed the principal heating element, the

resistance of which, at room temperature was about 5 ohms. An auxiliary coil of nichrome ribbon was wound around the outside of the block of asbestos strips in order to compensate for the cooling at the edges.

Below the hot plate was placed a sheet of copper two millimeters thick

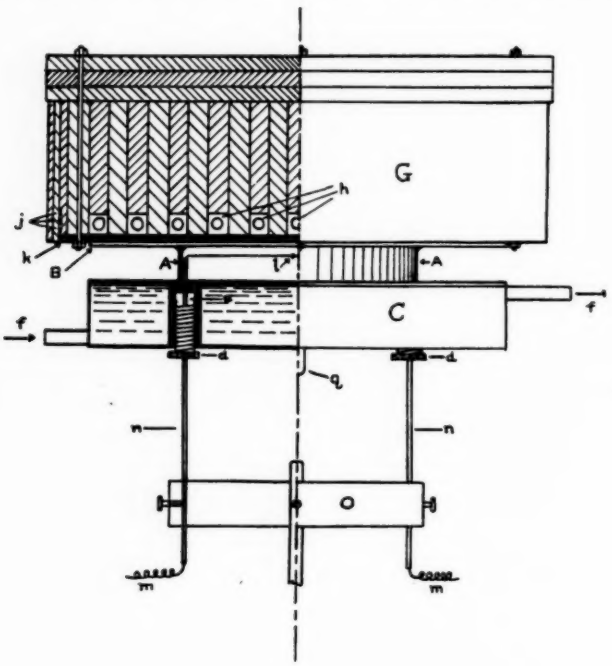


Fig. 1.

A, glass ring; *B*, glass plate; *C*, copper water-vessel; *ff*, water inlet and outlet; *e*, packing box; *d*, packing nut; *nn*, fine glass tubes; *l*, thermocouple; *o*, cross-arm; *mm*, thermocouple leads; *q*, side tubes carrying constantan wires; *g*, heater; *hh*, nichrome wire coils; *j*, auxiliary heating strip; *k*, copper equalizing plate. (Asbestos guard-ring strip removed to show details of apparatus.)

in order to equalize the temperature as much as possible. This sheet was in contact with a plate of glass, 14 cm. square and .17 cm. thick, which served as the top of the air chamber. To the glass plate was cemented a glass ring, 7.8 cm. internal diameter, 1.4 cm. high and .06 cm. thick. The cement used was "Vulcan Paste"[1] mixed with a little sodium silicate solution. This formed an airtight joint which withstood high temperatures. The lower edge of the glass ring was ground to give an airtight connection with a thick plate of copper, the surface of which was ground flat. This copper plate formed the top of a vessel through which water circulated.

[1] As supplied by the Pyrolectric Instrument Company of Trenton, N. J.

Temperatures were measured by means of a thermocouple made of 1 mil (.0025 cm.) constantan and 1.6 mil (.004 cm.) copper wires. The thermocouple was calibrated in steam, napthalene and sulphur vapors. The wires of the thermo-element were carried through small glass tubes which were moved up and down by means of a cross arm actuated by a micrometer screw. The temperature of the lower plate was given by two thermo-elements. The constantan wires of the latter were brought in through two tubes opening into the gas chamber just within the glass ring, where they were soldered to the copper plate. These tubes also served for introducing dry air or smoke into the chamber. An asbestos strip (not shown in diagram) closed the space between the upper and lower plates outside the glass ring, so that a guard ring was formed for the inner air vessel.

Any one of the thermo-elements could be connected with the rest of the circuit by means of suitable keys. The constant temperature junction common to all immersed in water and ice (or water only), in a Dewar flask. For the measurement of thermoelectric electromotive force a Kelvin-Varley slide, of total resistance 100,000 ohms, was used as a potentiometer with an Ayrton-Mather galvanometer. The error in temperature as indicated by the thermo-element was less than 0.3 per cent.

The distance of the centre of the thermo-element from the lower plate was determined by means of a cathetometer, the thermo-element being observed through the glass ring and small holes covered with mica in the asbestos outer casing. The error in determination of the height of the thermo-element was less than .02 mm. To allow for possible errors due to striae in the glass ring, a calibration was made. When the apparatus was cold the thermo-element was kept taut by small weights and its height adjusted by the micrometer screw which moved the cross arm. Readings taken on both micrometer screw and cathetometer agreed within the limits of observation. As the glass ring was in a uniform temperature gradient when the upper plate was heated, it was assumed that it introduced no error.

The current heating the upper plate was allowed to run for two or three hours to allow the temperature to attain a steady state before readings were begun. Although the voltage of the D.-C. circuit was not very steady, the temperature at a fixed point near the upper plate when at about 400° C., did not change by more than one or two degrees in two hours. This small progressive change could easily be allowed for in plotting curves.

A rough measurement of Q, the heat carried across the gas per square

centimeter per second, was also made. Thermocouples placed in the intake and outlet of the lower plate, gave the difference in temperature between the inflowing and outflowing water, while the water flowing through the apparatus in a given time was noted. The total flow of heat, so found, was divided by the total area of the glass plate. The above values of Q were only used in determining a radiation correction and were not required with any great accuracy.

CONVECTION.

The arrangement of the gas in layers of density diminishing with height tended to ensure stability. The guard ring was also of assistance in this regard. The temperature along horizontal planes was fairly uniform. The region within the ring was explored by a thermo-element moved along a horizontal plane over nearly two thirds of the breadth of the vessel. Variations of temperature were found to be less than 4° C., which could easily be accounted for by the errors in cathetometer settings. Tobacco smoke was blown into the vessel through one of the side tubes. The eddy motion quickly died out, and the smoke cloud was observed to settle gradually down to the bottom of the vessel in a well defined horizontal layer. No sign of movements due to convection could be noted. The agreement and reproducibility of the observations also indicate that convection was negligible in these experiments.

RADIATION.

The errors due to radiation, however, are not negligible. The thermo-element, at a temperature intermediate between those of the upper and lower plates, may be receiving more heat than it loses by radiation, and consequently its temperature will rise above that of the surrounding gas until the losses by conduction and convection, (*i.e.*, by "free convection"), equalize the gain by radiation. At other positions the thermo-element may be losing more heat by radiation than it receives, with the result that its temperature will fall below that of the surrounding gas.

A method was developed for determining the correction to be applied to the temperature indicated by the thermo-element, in order to find the temperature of the surrounding gas. As the detailing of this method would introduce too much matter foreign to the main object of this paper, its explanation is embodied in a separate paper, in which the application of the method to the present case is given in full.

OBSERVATIONS.

A series of observations of the temperature and height of the thermo-element was made at each of four different heating currents, *i.e.*, at four

different temperatures of the upper plate. As it soon became evident that radiation had an important effect on the temperature indicated by the thermo-element, the glass plate was silvered and four series of observations made using the same power inputs as before. The glass plate was then covered with soot and similar series of observations taken.

At a given heating current the number of observations made during a single run was between 20 and 40, the thermo-element being twice moved over the whole distance between the plates. The observations were plotted on a large scale with heights of the thermo-element above the lower plate as ordinates, and temperatures (referred to lower plate as zero) as abscissæ. When a smooth curve was drawn through these points they were found to lie on, or very close to, the curve.

Two series of observations were taken with the same current inputs, one with ordinary room air, and the other with air dried by passing through $CaCl_2$ and P_2O_5. One curve was found to fit both series of

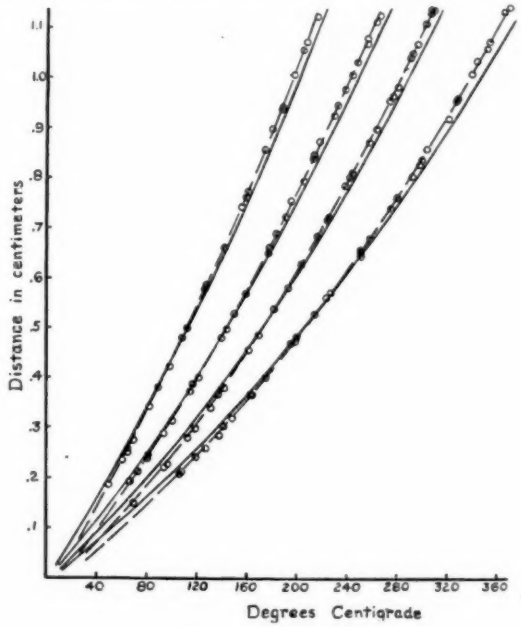


Fig. 2.

observations equally well. Furthermore no deviations from the curve could be found if the tubes leading to the gas chamber were open to the atmosphere, and in the latter experiments these tubes were left open.

As the actual observations are voluminous, they are not given in detail. As an example of the results obtained a specimen series of curves is shown in Fig. 2. In these experiments the glass was silvered. The

broken lines are smooth curves drawn through the points representing actual observations, while the unbroken lines are the same curves corrected for radiation by the method referred to.

It will be seen that the uncorrected curves do not pass through the origin, showing that a thermo-element indicates a temperature discontinuity at the boundary between plate and gas. The corrected curves however pass much closer to the origin. This is strong evidence that the corrections are of the right order of magnitude, for at atmospheric pressure no appreciable discontinuity is to be expected.

The results were tested on the assumption (2). If assumption (2) is correct, the temperature-distance curves (eq. 3) would be parabolic. In order to test this, temperatures were plotted as abscissæ, and distances from the lower plate divided by the corresponding temperatures as ordinates. The points were found to lie approximately on straight lines, showing that the curves were approximately parabolic. The values of α were at once obtained from these lines, since $\alpha = -2/c$, were c is the intercept on the axis of abscissæ. Fig. 3 is given as an example of the

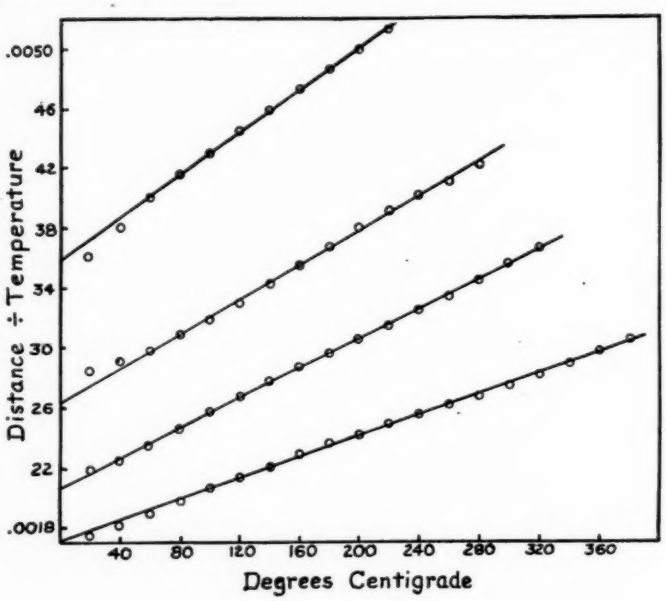


Fig. 3.

results obtained. The data used in Fig. 3 were taken from the corrected curves of Fig. 2.

The corrected curves of Fig. 2 were also tested on the assumption (4). On plotting T^{n+1} against z approximate straight lines were also obtained when a suitable value of n, chosen by trial and error, was used.

Thus the variation of the thermal conductivity of air with temperature seemed to be expressed by either assumption (2) or (4), within the limits of error imposed by the present experiments.

RESULTS AT HIGH TEMPERATURES.

The results obtained in these experiments are given in the following tables.

TABLE I.

Clear Glass.

Amperes.	α.	α'.	n.	T °C.	Cal. per Cm².	ϵ.
5.00	.00451	.00495	1.30	226	....	.50
6.35	.00457	.00564	1.20	318	....	.48
7.62	.00428	.00556	1.15	393	....	.40
8.42	.00517	.00644	1.12	438	....	.38

TABLE II.

Silvered Glass.

Amperes.	α.	α'.	n.	T °C.	Cal. per Cm².	ϵ.
5.00	.00394	.00394	1.32	277	.0418	.247
6.35	.00435	.00466	1.20	328	.0831	.374
7.62	.00488	.00550	1.17	393	.143	.464
8.42	.00445	.00466	1.05	456	.191	.432

TABLE III.

Blackened Glass.

Amperes.	α.	α'.	n.	T °C.	Cal. per Cm².	ϵ.
5.00	.00490	.00484	1.32	246	.0593	.544
6.35	.00544	.00602	1.30	319	.102	.523
7.62	.00500	.00572	1.12	413	.143	.407
8.42	.00500	.00600	1.12	483	.187	.363

The first column shows the current in amperes passing through the heating coil. In the second column are given the values of α determined from the corrected observations. For purposes of comparison, the column headed α' gives the values of the temperature coefficient obtained from the uncorrected observations. Values of n from the corrected observations are given in the fourth column. In order to show the range of temperature involved, the temperature of the upper plate, obtained by extrapolation of the curve, is shown in the fifth column. In the next column is shown Q, the quantity of heat carried across the gas, in calories per square centimeter. In the last column are given the values of ϵ, a

quantity determined from Q, as explained in the paper on the radiation error.

Unfortunately, measurements of Q were not made during the experiments with clear glass and the values of ϵ in this case are only estimated.

The only other investigation of the variation of K with θ for temperatures higher than 100° C. is that of Stafford.[1]

These results would give mean values of α over the range covered in the above experiments from .0030 to .0042.

It will be seen that the values of α given in Tables I., II., and III. are considerably higher than those which may be calculated from Stafford's experimental data.

The values of n are more concordant among themselves and decrease with increasing temperature range.

The values of α and n are dependent upon the corrections for radiation applied to the original curves, the corrections in some cases materially altering the original values. The probable errors involved in the assumptions made in evaluating the corrections are large. The largest error is probably in the value of the "effective diameter" of the wires of the thermo-element. In the process of fusing the wires a comparatively large lump of metal was unavoidably formed at the junction. The assumption was made that the effective diameter of the wires was that of the larger wire, viz., 1.6 mils. This value is very unlikely to be too large but may be considerably too small. An increase in the effective diameter of the wire would require larger corrections for radiation, which would decrease further the values of α. For instance, if the radiation corrections for the last series of observations for blackened glass (Table III.) had been doubled, the value of α would have been reduced from .00500 to .00357.

In view, then, of the uncertainties involved in the determination of the radiation corrections, the values of α given can be considered only as upper limits. From their variation with the temperature range it seems evident that a simple formula of the type

$$K = K_0(1 + \alpha\theta)$$

is not sufficient to express the variation of thermal conductivity with temperature over the range employed (20° to 500° C).

A formula of the form,

$$K = K_0(1 + \alpha\theta + \beta\theta^2)$$

would probably be needed to express approximately the variation of K with θ over this range, but with the uncertainty of the given values of α it would be futile to evaluate the coefficient β.

[1] Stafford, Zeits. für Phys. Chem., 77, p. 67, 1911.

Summing up the results of measurements of temperature gradients over a wide range, it may then be stated that a two power formula seems necessary in order to express approximately the variation of thermal conductivity of air with temperature. Owing to the errors involved in evaluating a correction for radiation, only upper limits to the first coefficient can be obtained from the present measurements. These values are given in the column headed α in Tables I., II. and III. above.

A formula of the form

$$K = K_0 T^n / T_0^n$$

also seems to express approximately the variation of K with temperature. The values of n obtained are given above. They are, however, not independent of the temperature range, and can be regarded only as upper limits owing to the uncertainty in the radiation corrections.

Temperature Coefficient between 15° and 100° C.

If the temperature range be decreased, the radiation corrections become smaller, and errors in them have less effect on the temperature coefficient. Accordingly experiments were carried out over the range 15° to 100° C.

The electrically heated plate was replaced by one of copper over which steam was made to circulate, while a potentiometer of low resistance was substituted for the Kelvin-Varley slide. The temperature of the lower plate was about 15° C. Both silvered and blackened plates were used.

The results obtained are given in Table IV.

Table IV.

Silvered Glass.		Blackened Glass.	
α.	α'.	α.	α'.
.00256	.00292	.00243	.00256
.00281	.00289	.00265	.00297

The mean of the given values of α is .00261.

As the value of α is small, slight variations in the shape of the curves have considerable effect on this value. Hence very close agreement in the individual values of α could not be expected and the variations shown in Table IV. may be considered as reasonable for this method. The probable error in the above value of α is about 4 per cent.

The mean value of α' is .00283. The introduction of the radiation correction thus lowers the value of the temperature coefficient 8.4 per cent. Over the range 15° to 100° C. the error due to radiation is thus

comparatively small and the temperature coefficient over this range should be measurable with much more accuracy than over the wider range. An error of nearly 50 per cent. in the radiation correction would only change the value of the temperature coefficient by about 4 per cent., which is approximately the accuracy afforded by the present measurements.

Some recent determinations of α by other observers over the range 0° to 100° C. are given below.

Eckerlein, *Ann. der Phys.*, 3, p. 120, 1900	.00362
Schwartze, *Ann. der Phys.*, 11, p. 303, 1903	.00253
Pauli, *Ann. der Phys.*, 23, p. 928, 1907	.00197
Eucken, *Phys. Zeits.*, 12, p. 1101, 1911	.00271
Mean of these values	.00271

Of these results the most trustworthy is that of Eucken, which agrees fortuitously with the mean of the four.

Thus it will be seen that the result of the present determination is in good agreement with the mean of other observers. This would show that the method described in this paper will give satisfactory results if the radiation corrections are relatively small, *i.e.*, if the temperature range is not too large.

REMARKS.

The satisfactory results obtained by this method when radiation corrections were small would indicate that by measuring the temperature gradients over a narrow range of temperatures the temperature variation of thermal conductivity might be determined up to a high temperature, in a series of steps.

There is also the possibility of using a small stretched wire as a resistance thermometer, instead of a thermocouple, and determining the radiation correction as before. This would have the advantage that a uniform wire might be used, doing away with the unavoidable lump of metal at the thermo-junction and thus making the effective diameter of the wire quite definite. The heat gained by the wire by radiation would still have to be calculated, however.

Experimentally, this method would have grave disadvantages, involving as it would, "line" instead of "point" temperatures. It would be necessary to keep the wire parallel to the plates, while the required potential leads would introduce further difficulties.

One point is clearly brought out in the present work, viz., the unreliability of temperatures as indicated by a temperature-measuring device placed in a gas in the presence of surfaces at temperatures differing considerably from that of the body of the gas.

The problem of temperature measurement in such cases is of considerable practical importance. That the radiation error involved may be large does not seem to have been emphasized in the past. In a publication recently received, however, Kreisinger and Barkley[1] discuss this point in considerable detail from the practical standpoint of the measurement of the temperature of gases in boiler settings. By using thermocouples of different diameters and exterpolating to zero diameter. Kreisinger and Barkley showed that the radiation error of a large thermocouple under practical working conditions might be as much as 150° C., in a gas at a temperature of about 1000° C.

In conclusion the writer wishes to express his thanks to Dr. L. V. King for placing the facilities of the Macdonald Physics Building at his disposal and for directing this research. He also wishes to express his gratitude to the Honorary Advisory Council for Scientific and Industrial Research of Canada, under whose auspices the earlier part of this work was done.

McGill University,
Montreal, Canada.

[1] Kreisinger and Barkley, Bull. U. S. Bureau of Mines, 145, 1918.

THE DETERMINATION OF THE RADIATION ERROR IN THE MEASUREMENT OF GAS TEMPERATURES. II.

BY G. H. HENDERSON.

SYNOPSIS.

Measurement of gas temperature.—Radiation error if the bounding surfaces are not all at the same temperature. A *mathematical expression* is derived which enables the radiation error to be determined for a thermo-element consisting of two wires of known diameter, if the radiant heat gained per second per unit length can be computed. It is based on Langmuir's equation for the heat loss by conduction and free convection. The author applies it to the case of a thermo-element between two parallel plates maintained at different fixed temperatures, and gives a table of corrections to be applied to thermo-elements of various diameters. The assumptions made are such that the probable error of a correction computed in this way may be large. *An alternative method of eliminating the radiation error* is that adopted by Kreisinger and Barkley. It consists in making measurements with a number of thermo-elements of decreasing diameter and in extrapolating from the results to the value which would be obtained with an element of zero diameter. This method is discussed and some *precautions* are suggested.

INTRODUCTION.

IF a volume of gas is enclosed by surfaces, some or all of which are at a temperature different from that of the gas, then in general, a thermo-element or other temperature measuring device immersed in the gas will not indicate the temperature of the gas at that point. The error is due to radiation. The thermo-element may be receiving more heat than it loses by radiation and consequently its temperature will rise above that of the surrounding gas until the losses by conduction and convection (*i.e.*, by "free convection") equalize the gain by radiation. On the other hand, the thermo-element may be losing more heat by radiation than it receives, with the result that its temperature will fall below that of the surrounding gas.

The difficulty of estimating the magnitude of this error was first met with by the writer in an investigation[1] of the temperature gradient in the air between two parallel planes maintained at different temperatures. The experimental arrangement consisted essentially of an upper hot plate and a lower cold plate, between which a volume of air was enclosed by a glass ring. The air between the plates was explored vertically by a small thermo-element. It is evident that with such an

[1] Henderson, PHYS. REV., 1919.

arrangement the thermo-element would not indicate the temperature of the gas on account of the radiation error, the indicated temperature being too low when the thermo-element was near the upper plate and too high when near the lower plate. On investigation it was found that the error was of the order of 15° C. when the thermo-element was near one or the other of the plates, which were maintained at temperatures of about 400° C. and 20° C. respectively.

The problem of the measurement of the temperature of gases, under conditions where the radiation error comes into play, is of considerable practical importance. It does not seem to have been emphasized in the past that the radiation error involved may be large, even for measurements made with no attempt at precision. In a publication recently received however, Kreisinger and Barkley[1] discuss this point in considerable detail from the practical standpoint of the measurement of the temperature of gases in boiler settings. These authors showed that the radiation error of a large thermo-element under practical working conditions might be as much as 150° C. in a gas at a temperature of about 1000° C.

A METHOD OF DETERMINING THE RADIATION ERROR.

In the investigation of temperature gradients referred to above, a method was developed for determining the correction to be applied to the temperature indicated by the thermo-element in order to find the temperature of the surrounding gas. This method is applicable in all cases where, from a knowledge of the temperature, dimensions and nature, of the surfaces and of the thermo-element, it is possible to calculate the heat gained by radiation per second by unit length of the thermo-element. In many cases heat will be lost by radiation, but to avoid repetition a gain of heat only will be referred to in the following.

If T_2 be the temperature of a heated wire suspended in still air,

T_1 be the temperature of the surrounding air,

K be the thermal conductivity of air,

and

$$\varphi_2 = \int_0^{T_2} K d\theta, \qquad \varphi_1 = \int_0^{T_1} K d\theta,$$

where θ denotes temperature on any convenient scale, then it has been shown by Langmuir[2] that the heat loss, W_c, by conduction and convection (*i.e.*, by "free convection") per second per centimeter length

[1] Kreisinger and Barkley, Bull. U. S. Bureau of Mines, 145, 1918.

[2] Langmuir, PHYS. REV., 34, p. 401, June, 1912. Trans. Am. El. Chem. Soc., p. 299, 1913. Trans. A. I. E. E., p. 1229, 1912.

of wire, is given by the formula

$$W_c = S(\varphi_2 - \varphi_1), \tag{1}$$

where S is a "shape factor" given by the equation

$$\frac{a}{B} = \frac{S}{\pi} e^{-(2\pi/S)}, \tag{2}$$

where a is the diameter of the wire and B is .43 cm. for air at atmospheric pressure and room temperature.

If W_R is the radiant energy, in watts, gained per second by one centimeter of the wire, then in the steady state we have $W_R = 4.19\, W_c$ and we may thus write

$$W_R = 4.19\, S(\varphi_2 - \varphi_1). \tag{3}$$

Treating the thermo-element as a uniform wire, S and φ_2 are at once determined, hence if W_R may be calculated, φ_1 is given from (3) and finally T_1, the temperature of the surrounding gas.

APPLICATION OF THE METHOD.

The use of this method in the investigation of the temperature gradient in air between parallel planes is given below as an example. The problem here presented was to obtain the radiation correction which should be applied to the temperature indicated by a thermo-element placed between parallel plates maintained at different temperatures. With a small thermo-element, which would not appreciably disturb the temperature gradient, this was equivalent to finding the temperature of the surrounding gas.

It was first necessary to calculate W_R. The plates of the apparatus used were 7.8 cm. in diameter and 1.4 cm. apart but the glass ring acted somewhat as a continuation of the plates as regards radiation to the thermo-element. Consequently as a first approximation both the upper and lower plates were considered to be infinite in extent.

If we take a small element ds of the surface of the wire, considered as a black body, the radiant heat received by ds from element of surface of the upper plane subtending a solid angle $d\omega$ at ds is $S_4 \cos\theta d\omega ds$, where S_4 is the total emmission of heat from unit surface of the upper plane and θ is the angle between the normal to ds and the axis of the elementary solid angle $d\omega$.

On integrating this expression over the upper plane it may be shown that the heat received by ds from the upper plane is

$$\frac{1 + \cos\alpha}{2} S_4 ds,$$

where α is the angle between the normals to the plane and to ds.

Integrating first around a narrow ring of the surface of the wire and then along unit length of the wire, assuming the radiation to be uniform along the axis, it is easy to show that the heat received by unit length of the wire from the upper plate is $(\pi a/2)S_4$. Similarly the heat lost by unit length of the wire to the upper plate is $(\pi a/2)S_2$, where S_2 is the total emission from unit area of the surface of the wire.

Hence the resultant gain of heat by unit length of the wire from the upper plate is $(\pi a/2)(S_4 - S_2)$.

Similarly the resultant gain of heat by unit length of the wire from the lower plate is $(\pi a/2)(S_3 - S_2)$, where S_3 is the total emission from unit surface of the lower plate.

Hence the total gain of radiant heat by unit length of the wire is

$$W_R = \frac{\pi a}{2}(S_4 + S_3 - 2S_2).$$

To determine W_R it was then necessary to evaluate S_2, S_3 and S_4.

The wires of the thermo-element were highly oxidized and their surfaces could be considered to be approximately black body surfaces as assumed above. By Stefan's law, the total emission S_2 is given by $S_2 = \sigma_2 T_2^4$ watts per square centimeter where T_2 is the absolute temperature of the thermo-element and $\sigma = 5.7 \times 10^{-12}$.

The surface of the lower plate of copper was slightly oxidized. The term S_3 contributed by it to the expression for W_R was always comparatively small and was assumed to be $.756T_3^4$, where T_3 was the absolute temperature of the lower plate. This expression was shown by Langmuir[1] to express approximately the total emission from oxidized copper.

The heat emission from unit surface of the upper plate was assumed to be given by $S_4 = \epsilon\sigma T_4^4$, where T_4 was the absolute temperature of the upper plate and ϵ a factor less than unity, which was itself a function of T_4. The value of ϵ was determined experimentally for the different values of T_4 used in the experiments. The total quantity of heat transferred from the upper hot plate to the lower cold plate was found approximately from the rate of flow and the in-going and out-going temperatures of the water used to cool the lower plate. The quantity of heat transferred by conduction through the air between the plates was then calculated. For this purpose a value of the thermal conductivity of air, K, at the mean temperature of the air between the plates was used. This was assumed to be given by

$$K = K_0(1 + \alpha\theta),$$

[1] Langmuir, Trans. Am. El. Chem. Soc., p. 321, 1913.

where K_0, the thermal conductivity of air[1] at 0° C., $= 5.22 \times 10^{-5}$, α, the temperature coefficient[2] of $K = .0027$, and θ the temperature in degrees centigrade. The quantity of heat so calculated, usually small, was subtracted from the total heat transfer. The difference represented heat transmitted by radiation and the amount of the radiant heat per unit area of the plates was equal to $(\epsilon\sigma T_4^4 - .75\sigma T_3^4)/4.19$ calories per square centimeter. All other terms being known, ϵ was readily found and hence W_R. The values of W_R were tabulated for a number of thermo-element temperatures.

The value of S was calculated by trial from equation (2). For a wire of 1.6 mils (.004 cm.) diameter the value of S was 1.57.

When computing values of φ, instead of assuming K to vary with the temperature according to Sutherland's formula, as was done by Langmuir, the assumption was made that

$$K = K_0(1 + \alpha\theta)$$

where K_0 and α have the values quoted above.

There does not seem to be more experimental justification for using one formula rather than the other, while the form adopted here makes computation easier.

The function $4.19S\varphi$ was then plotted against the corresponding temperature on cross-section paper.

In computing the radiation correction the function $4.19S\varphi_2$ corresponding to a chosen thermo-element temperature T_2 was found from the curve. The heat gain W_R was then taken from the table. By (3)

$$4.19S\varphi_1 = 4.19S\varphi_2 - W_R.$$

Hence $4.19S\varphi_1$ was at once found and finally the corresponding temperature T_1 of the gas surrounding the thermo-element was found from the curve. The radiation corrections thus involved were found to be quite large, varying from + 12° C. near the upper plate to − 15° C. near the lower plate, when the plates were not polished and radiation was consequently most effective.

A check on the accuracy of these corrections was obtained in the following way. In Fig. 2 of the writer's[3] paper on temperature gradients, the heights of the thermo-element above the lower plate were plotted as ordinates and the corresponding temperatures indicated by the thermo-element were plotted as abscissæ for the broken curves, the temperature of the lower plate being taken as zero. The unbroken curves

[1] Hercus and Laby, Proc. Roy. Soc., A, 668, p. 190, 1919.

[2] Eucken, Phys. Zeits., 12, p. 1101, 1911.

[3] Henderson, Phys. Rev., 1920.

had the same ordinates as before but the abscissæ represented temperatures corrected for radiation as outlined above. The uncorrected curves did not pass through the origin, showing that a thermo-element indicated a temperature discontinuity at the plate. The corrected curves, however, passed much closer to the origin. This was regarded as strong evidence that the corrections were of the right order of magnitude, for at atmospheric pressure no appreciable discontinuity was to be expected.

In connection with this example three points deserve notice.

1. A number of assumptions were made in evaluating the radiation corrections and the probable errors involved in these assumptions were large, so that great accuracy in the corrections was not to be expected. The largest error was probably in the value of the effective diameter of the wires of the thermo-element, which was made of 1 mil (.0025 cm.) constantan and 1.6 mil (.0040 cm.) copper wires. In the process of fusing the wires a comparatively large lump of metal was unavoidably formed at the junction. The assumption was made that the effective diameter of the wires was 1.6 mils (.0040 cm.), the diameter of the larger, copper wire. This value was unlikely to be too large, but might have been considerably too small. The shape factor S was only slightly affected by changes in the diameter of the wire, but the heat gained by radiation, W_R, was proportional to the diameter. An increase in the effective diameter of the wire thus required larger radiation corrections. It was noticeable that slightly larger radiation corrections would have caused all the corrected curves referred to above to pass through the origin.

2. The term B of equation (2), while independent of the temperature of the wire, probably depended upon the temperature of the air. It was stated by Langmuir that B varied roughly in inverse proportion to the density, and therefore in proportion to the temperature. As S was affected only slightly by changes in B, the variation of S with the temperature of the air was neglected, in view of the uncertainty as to the exact law governing B.

3. Langmuir's theory was only shown to express the facts in a gas of uniform temperature. The layer of stagnant gas which Langmuir assumed to surround the wire, if it had any physical significance at all, would be distorted by the temperature gradient. However the mean thickness would have been about the same as that of an undistorted layer, leaving S unaltered. It was assumed that the temperature of the surrounding gas, as given by the above method, was the temperature of the gas on a horizontal layer passing through the centre of the thermo-element.

ANOTHER METHOD OF ELIMINATING THE RADIATION ERROR.

In the method outlined above, it is necessary to calculate W_R, the heat received by radiation by one centimeter of the thermo-element wire, to the same accuracy as is desired in the corrections. In practical problems this can seldom be done and the method in most cases is therefore in applicable.

Another method of eliminating the radiation error is that used by Kreisinger and Barkley.[1] These authors were confronted with the problem of measuring the temperature of the gases in boilers. Here the hot gases were surrounded by the cooler walls of the boiler, and the radiation error was large. In addition the gases were in motion. Kreisinger and Barkley adopted the method of using several thermo-elements of different sizes, plotting the indicated temperatures against the diameters of the thermo-elements and extrapolating to a wire of zero diameter. The temperature for a wire of zero diameter, as determined by the curve was taken as the temperature of the gas. The same method was used earlier by Nichols[2] for determining the temperatures of small flames, such as that of an acetylene burner, when the loss of heat from the junction along the thermo-element wires was so great as to cause a considerable error in the indicated temperature of the flame. In many cases, when a considerable length of wire on either side of the junction is immersed in gas of uniform temperature, this error becomes negligible.

It is possible by the method given in this paper, to predict the results obtainable from thermo-elements of different diameters, when immersed in a gas at rest and subject to this radiation error. The effect of motion of the gas, for small velocities would not appreciably affect the results, as may be seen from the results of investigations by King[3] and Kennelly[4] on the loss of heat from small wires in a stream of gas. The radiant heat received by one centimeter of a thermo-element wire exposed to radiation from neighboring surfaces is approximately proportional to its diameter. Consider for instance a thermo-element losing, in watts per centimeter, a quantity of radiant heat, equal numerically to its diameter in centimeters. Such a condition is to be found for instance, when a thermo-element wire is placed between and parallel to two planes in such a position that it indicates a temperature of 320° C., when the temperature of the upper plane is 450° C. and that of the lower plane is 30° C. It should be noted that in practical measurements, such as

[1] Kreisinger and Barkley, Bull. U. S. Bureau of Mines, 145, 1918.

[2] Nichols, PHYS. REV., 10, p. 234, 1900.

[3] King, Trans. Roy. Soc., A, 520, 1914.

[4] Kennelly, Trans. A. I. E. E., 26, p. 969, 1907; 28, p. 368, 1909.

those of the temperatures of the gases, the heat gains or losses and consequent radiation errors will often be larger than the value assumed above.

The corrections to be applied for thermo-elements of different sizes are shown in Table I. The first column gives the diameter of the wire

TABLE I.

a, Cms.	a, Inches.	S.	Corrections.
.0031	.00123	1.5	5.2
.0118	.00464	2.0	14.6
.0277	.0109	2.5	27.5
.0505	.0199	3.0	41.6

in centimeters, the second the same diameter in inches, the third the value of S and the fourth the corrections in degrees centigrade, calculated according to the above method.

The results are also shown graphically in Fig. 1. Langmuir's theory

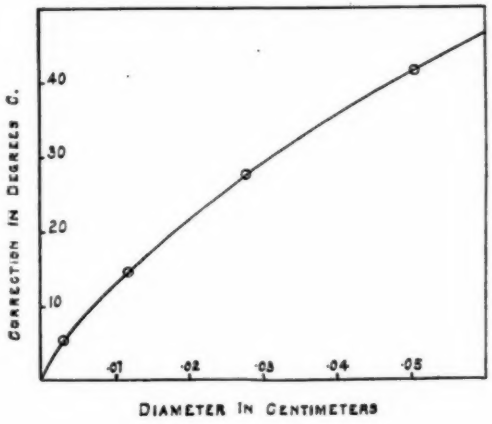


Fig. 1.

has only been verified for wires ranging in diameter from .05 down to .004 centimeter, but it seems reasonable to suppose that the theory would hold for smaller wires and that the curve would pass through the origin. It will be seen that the curve drops somewhat sharply towards the origin. This shows the danger of using wires of large diameters only. *If the method of extrapolating to a wire of zero diameter is to be used, care should be taken that wires of small diameter are included in the range of sizes used. If possible, wires of .0025 or .005 centimeters diameter (1 or 2 mils) should be used.* Care should also be taken that a length of wire be left on

either side of the junction, free from the supporting frame to minimize radiation. The necessity of using wires of small diameter becomes greater when consideration is taken of the unavoidable fused lump of metal formed at the junction, as this adds to the effective diameter of the wire and makes extrapolation more uncertain.

In conclusion the author wishes to express his thanks to Dr. L. V. King for his helpful advice.

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IS THE EINSTEIN RADIATION FACTOR h A CONSTANT?

BY FERNANDO SANFORD.

SYNOPSIS.

K-Series of characteristic X-rays; theory assuming orbital motion of the radiating electron.—By combining the equation for orbital motion of an electron about a central positive charge and the Einstein photoelectric equation with the following equation for the nuclear charge, $q = 2e(N - 3.6)$, the author gets an equation of the form of Moseley's equation, which gives values of λ for the elements from bromine (35) to cerium (58) which agree closely with the observed wave-lengths of the K-radiation. In this calculation, however, h^3/m is assumed constant. Now since the mass of the electron m varies with the speed, if h is constant the ratio h^3/m is not constant and the measured wave-lengths can no longer be computed from the above equation. *Deduction.* The author presents this as evidence that the *quantum constant h varies with the frequency.*

Relation between the β-and γ-rays of RaB; theory.—Assuming the speed of the β-rays is their orbital speed before emission and that the Einstein photoelectric equation gives the relation between the energy of a β-ray and the frequency of the corresponding γ-radiation, the author computes the wave-lengths of the γ-rays corresponding to the various β-rays of RaB. The values differ according to whether h or h/m is assumed to be constant. The agreement between calculated and observed wave-lengths is not striking in either case, but is better if h/m is constant. *Deduction.* This suggests that the *quantum constant h varies with the frequency.* The author does not discuss the discrepancy between the conclusions derived respectively from X-ray and γ-ray data, though it is obvious that h^3/m and h/m cannot both be constant.

IT is well-known that when electrons are expelled from metals under the stimulus of ultra-violet light or X-rays or when X-rays are induced by the impact of rapidly moving electrons upon any substance the equation $Ve = \frac{1}{2}mv^2 = h\nu$ gives a measure of the energy of the ejected or impinging electron in terms of the wave frequency of the inducing or induced radiation.

I have shown elsewhere[1] that by combining the equation for orbital motion of an electron about a central positive charge, viz., $mv^2/R = Qe/R^2$, with the equation $\frac{1}{2}mv^2 = h\nu$ it is possible to compute the central positive charge of a radiating atom from the equation $Q = 2^{1/2}h^{3/2}c^{1/2}/m^{1/2}e\pi\lambda^{1/2}$. By using the commonly accepted values of m, h, e and c this equation reduces to the form $Q = 2.882 \cdot 10^{-12}/\sqrt{\lambda}$. By combining this equation

[1] See especially "On The Nuclear Charges of Atoms," PHYS. REV., IX., 383 (1917); "The Astronomical Atom and the Spectral Series of Hydrogen," Astrophysical Journal, XLVIII., 1 (1910); "The Helium Spectrum and the Unit Electrical Charge," Astrophysical Journal.

with the Moseley equation it has been found possible to compute the wave-lengths of all the characteristic X-ray bands, and by combining it with the Ritz equation for spectral series, to compute the wave-lengths of all the known lines in the spectral series of hydrogen and helium in terms of the unit electrical charge and the serial numbers of the respective lines.

It is also possible on the same assumption of orbital motion of the radiating electron to calculate the value of h from the convergence charge of the Balmer series in hydrogen.

In the wave-length measurements of K-radiation made by Blake and Duane,[1] the values of Q calculated from the above equation are found to be equal to the atomic charges of the same elements calculated from the Moseley formula by the equation $Q = 2e\ (N - 3.6)$, where N is the atomic number. By combining the two equations the wave-length for each element may be calculated from the equation

$$\lambda = \left[\frac{2.882 \cdot 10^{-12}}{2e(N - 3.6)}\right]^2.$$

The results of this calculation may be seen in Table I. The charges are in electrostatic units and are multiplied by 10^{10}. The wave-lengths are multiplied by 10^{8}.

TABLE I.

Element.	N.	Q.	λ, Calc.	λ, Obs.
Cerium	58	5.194	.3071	.3073
Lanthanum	57	5.10	.3189	.3188
Barium	56	5.00	.3318	.3307
Cæsium	55	4.91	.3441	.3444
Iodine	53	4.72	.3721	.3727
Tellurium	52	4.62	.3887	.3896
Antimony	51	4.525	.4051	.4065
Tin	50	4.43	.4225	.4242
Indium	49	4.335	.4413	.4434
Cadmium	48	4.24	.4615	.4632
Silver	47	4.143	.4830	.4850
Palladium	46	4.05	.5062	.5075
Rhodium	45	3.952	.5314	.5324
Ruthenium	44	3.86	.5565	.5584
Molybdenum	42	3.668	.6168	.6180
Niobium	41	3.57	.6512	.6503
Zirconium	40	3.475	.6872	.6872
Yttrium	39	3.38	.7259	.7255
Strontium	38	3.285	.7691	.7696
Rubidium	37	3.19	.8154	.8143
Bromine	35	3.00	.9216	.9179

[1] PHYS. REV., X., 702 (Dec., 1917).

In the calculation of Q in Table I., the value of h is taken as $6.55 \cdot 10^{-27}$ and the value of m as $9.02 \cdot 10^{-28}$. If we compute the orbital velocity of the electrons from the same equations, we find $v^2 = hc/m\lambda$, and $v = 6.60 \cdot 10^5/\sqrt{\lambda}$. If we calculate a value of v from this equation and then correct the value of m from the equation

$$m = m_0 \Big/ \sqrt{1 - \frac{v^2}{c^2}},$$

we shall find that for even the lowest values of N for which wave-lengths were measured by Blake and Duane the value of Q is appreciably smaller than when calculated on the assumption that m is constant. Furthermore, the value of Q obtained in this way can no longer be used in calculating λ by means of the Moseley equation.

Perhaps this can be shown as well as any way by calculating the value of b in the equation $Q = 2e(N - b)$ from the two sets of values of Q. This is done in Table II. for the elements whose wave-lengths are given in Table I.

TABLE II.

N.	Q_1.	Q_2.	$Q_1/2e$.	$Q_2/2e$.	$N-Q_1/2e$.	$N-Q_2/2e$.
58	5.194	4.99	54.4	52.2	3.6	5.8
57	5.10	4.89	53.4	51.3	3.6	5.7
56	5.00	4.81	52.4	50.4	3.6	5.6
55	4.91	4.73	51.4	49.5	3.6	5.5
53	4.72	4.56	49.4	47.7	3.6	5.3
52	4.62	4.46	48.4	46.7	3.6	5.3
51	4.525	4.38	47.4	45.9	3.6	5.1
50	4.43	4.30	46.4	45.0	3.6	5.0
49	4.335	4.21	45.4	44.1	3.6	4.9
48	4.24	4.12	44.4	43.1	3.6	4.9
47	4.143	4.03	43.4	42.2	3.6	4.8
46	4.05	3.95	42.4	41.4	3.6	4.6
45	3.952	3.86	41.4	40.4	3.6	4.6
44	3.86	3.77	40.4	39.5	3.6	4.5
42	3.608	3.59	38.4	37.6	3.6	4.4
41	3.57	3.50	37.4	36.6	3.6	4.4
40	3.475	3.41	36.4	35.7	3.6	4.3
39	3.38	3.32	35.4	34.8	3.6	4.2
38	3.285	3.23	34.4	33.75	3.6	4.25
37	3.19	3.14	33.4	32.9	3.6	4.1
35	3.00	2.96	31.4	31.0	3.6	4.0

In Table II., Q_1 is the charge calculated in Table I., while Q_2 represents the charge calculated from the same equation assuming h to be a constant and correcting m for velocity. These quantities divided by $2e$ give the quantity $N - b$.

Table II. shows conclusively that if the mass of an electron varies as its velocity varies, its rate of emission must also vary, or else the Moseley equation does not apply to the charges calculated on the assumption of orbital motion. That the Moseley equation does apply so completely to the charges calculated on the assumption that $h^{3/2}/m^{1/2}$ remains constant is an argument against the hypothesis that h is constant.

It seems reasonable that if h is a rate of electromagnetic energy emission it should increase with an increase of the electromagnetic field of the radiating electron, as seems to be indicated by the above computations. In order to determine more definitely whether it does so increase, it is desirable to know both the orbital speed and the radiation frequency of some radiating electron of sufficiently high velocity to have a greatly increased electromagnetic mass. Such high speeds seem to be possessed only by the β-rays expelled from radioactive substances.

In the light of what has been said above, it seems extremely probable that the speeds of electrons expelled under the stimulus of ultra-violet light or X-rays must be the orbital speeds which they possessed at the instant of breaking away from their respective atoms. If this be the true explanation of their velocities of emission, and no one seems to have proposed any other reasonable explanation, it seems almost certain that the same explanation must account for the speeds of the β-particles expelled by radioactive bodies. This would require that the Einstein photoelectric equation should hold for the energies of the expelled β-rays and the frequencies of the accompanying γ-radiations from the same element.

Rutherford and his colleagues have spent much time on the investigation of this question, and are of the opinion that such a relation does,

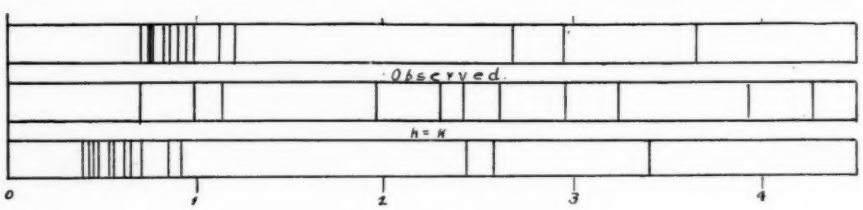

Fig. 1.

Observed spectrum of Radium *B* add Radium *C* compared with spectra computed for Radium *B*.

indeed, hold, and that some of the γ-rays from Radium-*B* and Radium-*C* are the true *K*- and *L*-radiation bands of these elements.[1] This view would seem to be further strengthened by the fact that several of the

[1] The Connection Between the β and γ Ray Spectra, Phil. Mag., XXVIII., 305–319.

velocities determined for the β-rays from Radium-B and Radium-C agree with the orbital velocities computed from the measured wave-lengths of the γ-radiation from these elements.

On page 316 of the article referred to above Rutherford gives the velocities of fourteen different groups of β-rays expelled from Radium-B. In a paper by Rutherford and Andrade on "The Spectrum of the Penetrating γ-Rays from Radium B and Radium C"[1] is given a table of the wave-lengths of fourteen different lines in the γ-ray spectrum of these elements. From these data it is possible to calculate the wave-lengths corresponding to the different velocities of β-rays, using the equation $\nu = mv^2/2h$, and to compare the wave-lengths so calculated with the observed wave-lengths of the γ-radiation from Radium-B and Radium-C.

In this calculation, if h remains constant while m varies with the electron velocity we have $m = m_0/\sqrt{1-\beta^2}$, where m_0 = the mass of an electron at low speeds and $\beta = v/c$, where c is the velocity of light. Assigning the values usually given to m_0 and h, this equation becomes $\nu = .0685v^2/\sqrt{1-\beta^2}$.

If, on the other hand, m/h remains constant, $\nu = .0685v^2$.

In the table below are given the values of λ calculated by each of these

TABLE III.

β.	$\lambda \cdot 10^3$, h = Const.	$\lambda \cdot 10^3$, m/h = Const.	$\lambda \cdot 10^3$, Obs.
.823	.408	.720	.71
.805	.445	.755	.99
.797	.463	.767	1.15
.787	.485	.785	1.37
.762	.543	.838	1.59
.751	.569	.862	1.69
.731	.620	.910	1.96
.719	.657	.944	2.29
.700	.710	.99	2.42
.656	.853	1.13	2.62
.635	.935	1.21	2.96
.426	2.44	2.68	3.24
.414	2.58	2.84	3.93
.365	3.40	3.65	4.28

equations for the fourteen values of β given in Rutherford's paper, and in the fourth column are given the values of λ as measured by Rutherford and Andrade from the γ-radiation of Radium-B and Radium-C.

It may be seen from the above table that there is no close correspondence between either series of calculated values of λ and the observed

[1] Phil. Mag., XXVIII., 263–273.

values. It will be seen, however, that the correspondence is much the better with the series calculated on the assumption of the constancy of the ratio m/h. This series begins with the observed series and three of the fourteen lines agree perfectly with observed lines while two others are within the limits of possible error in measurement. The series calculated on the assumption of the constancy of h, on the other hand, has eight of its fourteen lines of shorter wave-length then any that have ever been measured and only two lines which correspond at all closely with observed lines.

Rutherford gives reasons for believing that the lines 1.37, 1.59 and 1.69 are due to Radium-*C*, and others of the observed lines may be due to this element. If these lines be taken out and the three series be plotted to scale as is done in Fig. 1, the correspondence of the observed series with the series based upon the constancy of the ratio m/h is, at least, strongly suggestive, even though far from conclusive.

STANFORD UNIVERSITY,
June 25, 1919.

ADDED NOTE BY AUTHOR.—Since this article was accepted by THE PHYSICAL REVIEW Siegbahm and Göussen have published wave-length measurements of *K*-radiation for elements of atomic number to $N = 92$. It is found that for elements of atomic number higher than 58 Moseley's equation does not apply, and h^3/m is no longer approximatly constant but apparently h varies as log m. On this assumption nine of the fourteen lines in the γ-ray spectrum of $Ra - B$ and $Ra - C$ may be definitely referred to their respective β-radiations. The argument for the variability of the factor h seems conclusive.